



Universidad Autónoma
de Madrid

Biblos-e Archivo
Repositorio Institucional UAM

Repositorio Institucional de la Universidad Autónoma de Madrid

<https://repositorio.uam.es>

Esta es la **versión de autor** del artículo publicado en:
This is an **author produced version** of a paper published in:

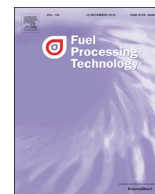
Fuel Processing Technology 212 (2021): 106639

DOI: <https://doi.org/10.1016/j.fuproc.2020.106639>

Copyright: © 2020 Elsevier B.V. This manuscript version is made available under the CC-BY-NC-ND 4.0 licence <http://creativecommons.org/licenses/by-nc-nd/4.0/>

El acceso a la versión del editor puede requerir la suscripción del recurso

Access to the published version may require subscription



Research article

Multiscale evaluation of CO₂-derived cyclic carbonates to separate hydrocarbons: Drafting new competitive processes

Elisa Hernández, Rubén Santiago, Cristian Moya, Pablo Navarro*, José Palomar

Departamento de Ingeniería Química, Universidad Autónoma de Madrid, Madrid, Spain

ARTICLE INFO

Keywords:

Cyclic carbonates
Extractive distillation
Liquid-liquid extraction
COSMO-RS
Aspen Plus

ABSTRACT

Current chemical technologies present a negative impact on society and environment since they are based on processes that demand large energy and the use organic solvents, entailing relevant carbon footprint. Emerging solvents impose additional criteria in the design of new separation technologies. Aiming at addressing favorable solvent properties but also reducing emissions of carbon dioxide, cyclic carbonates are CO₂-based synthesizable designer solvents unexplored in the literature. Cyclic carbonates are a new class of tunable compounds with ability to enhance current standards and improve the sustainability of processes. Here a comprehensive and systematic study, covering fundamental and process scale insights, is developed on the use of cyclic carbonates in the most relevant hydrocarbon separations in the literature, namely {*n*-heptane + toluene}, {cyclohexane + benzene} and {cyclohexane + cyclohexene} by liquid-liquid extraction and extractive distillation. A *priori* COSMO-RS method described the driving interactions between cyclic carbonates and hydrocarbons, whereas COSMO-based/Aspen was used to further inspect phase equilibria and design liquid-liquid extraction and extractive distillation separation processes, using benchmark industrial solvents (sulfolane and *N*-formylmorpholine). The favorable process performance starts a new research line to fine-tune cyclic carbonates' structure, but currently drafting feasible approaches, competitive or even better when compared with conventional solvents.

1. Introduction

Separation processes in the oil industry present a negative environmental impact due to their old-fashioned optimization criteria. This is translated into high-energy demands in regeneration stages and the use of volatile, toxic and non-sustainable solvents [1]. Moreover, CO₂ emissions related to the main and secondary processes that allow the industrial separation should also be considered [2]. Currently, scientific community must impose the use of more sustainable technologies combining excellent performance with minimum environmental impact to enhance traditional industrial technologies. This allows addressing new quality standards at a more sustainable level [2].

Among other examples, hydrocarbon separations are one of the target kind of mixtures at which scientific interest is focused [3,4]. It is widely remarkable the interest in: (i) aromatic/aliphatic separation, aiming at separating BTX from reformer and pyrolysis gasolines [1,5–7]; (ii) cyclohexane/benzene and cyclohexane/cyclohexene separations because of their coexistence in their production [8–10].

The aromatic/aliphatic separation is a key separation in the oil industry, traditionally accomplished by Sulfolane® and Morphylane®

processes, comprising liquid-liquid extraction and extractive distillation technologies [11]. Concerning the cyclohexane-cyclohexene-benzene matrix of binary separations, there are similar processes involving extractive distillation and liquid-liquid extraction processes, employing similar solvents as those used in the aromatic/aliphatic separation [12,13].

In last decades, efforts are being focused on designing alternative new generation substances with certain improvements when compared with conventional solvents, being of especial interest when reviewing hydrocarbon separation. From a long list, ionic liquids and eutectic solvents have been studied in last years.

Ionic liquids (ILs) have been widely investigated for the aromatic/aliphatic separation due to their favorable solvent properties (low volatility, designer solvent ability, high thermal and chemical stability and wide liquid range) [14,15]. It was demonstrated that some ILs, as those based on [TCM][−] anion [5], coordinated transition metals with CN groups [16] or well-selected IL binary mixtures [17], can be competitive against sulfolane for liquid-liquid extraction, in terms of distribution ratio and selectivity despite their 2–3-time differences on viscosity values [1]. However, aromatic commercial standards are not

* Corresponding author.

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

<https://doi.org/10.1016/j.fuproc.2020.106639>

Received 18 July 2020; Received in revised form 21 September 2020; Accepted 11 October 2020

Available online 19 October 2020

0378-3820/ © 2020 Elsevier B.V. All rights reserved.

fulfilled at the same time a feasible process is designed [6]. For this reason, extractive distillation was also studied as an alternative separation. Experimental work showed that, again, [TCM][−] based ILs present the best performance as entrainers, improving the separation results obtained from liquid-liquid extraction operation [5]. Cyclohexane/benzene separation using ILs has been also studied [18]. Once again, cyano-based ILs stand out among the others, revealing a competitive behavior compared to conventional solvents in extractive distillation technology [9]. Concerning cyclohexane/cyclohexene separation, liquid-liquid extraction was discarded as an alternative since it cannot reach purity nor recovery standards using ILs [9]. However, extractive distillation using cyano-based ILs offered a suitable way to perform the separation [9]. Therefore, ILs appear as an alternative to separate hydrocarbons, designing liquid-liquid extraction and extractive distillation processes. However, their limited transport properties because of their high viscosity values, high prize, and environmental concerns [19] suggest the possibility of searching new solvents able to fulfill the specifications as well as overcoming the current challenges related to the scale-up of ILs-based processes.

Eutectic solvents, frequently identified as deep eutectic solvents, are another class of new solvents that are being proposed in liquid-liquid extraction and even in extractive distillation designs [13,20,21]. In addition to environmental concerns, the low cost related to these new generation solvents stands as an ideal design basis [22]. Their viability in aromatic/aliphatic separation was demonstrated, but without reaching commercial purities [6]. Nonetheless, distillation processes that aim to regenerate eutectic solvents from the extract or residue stream draw a temperature profile that is near their thermal stability limitations [6,23]. This allows working within a narrow liquid range because of their high melting points and low thermal stability and/or partial evaporation of their constituents. For all these reasons, eutectic solvents have not become, at the moment, a real alternative to the solvents typically used to separate these mixtures.

Therefore, the search continues trying to find other environmentally friendly and abundantly available low cost new solvents [2]. Cyclic carbonates are polyvalent and emerging bio-solvents at industry, ranging from reaction media to precursors in the synthesis of polycarbonates [24]. There are different processes to produce carbonates such as from urea or glycerol [2,25,26]. CO₂ cycloaddition reactions from epoxides and similar instable compounds show a new strategy to synthesize cyclic carbonates and also consuming CO₂, which involves minimizing its emissions at the same time that value-added products are generated [27,28]. Biomass derived terpenes can also be converted into cyclic carbonates by catalytic coupling with CO₂ [29], which allows the synthesis of cyclic carbonates from completely natural and renewable sources. Moreover, olefins derived from fatty acids present in biodiesel production constitute a renewable feedstock that can be converted into a wide variety of different functionalized cyclic carbonates by direct oxidative carboxylation [30–32]. At this time, the use of epoxides imposes high energy demand in their synthesis, which can be mitigated by properly selecting these new generation reactants, from natural sources or produced at biorefineries [26,29]. In any case, the use of CO₂ as a C1 building block improves the sustainability of cyclic carbonates productions, but the search of new applications for these carbonates remains important to successfully design an integral strategy to improve CO₂ emissions and industrial separation processes.

Among other possibilities, cyclic carbonates present interesting features as solvents: (i) low volatile character [24,33]; (ii) tunable structure depending on the functional groups integrating the epoxide or related reactant [34]; (iii) low viscosity [33]; (iv) potential high availability and low price as a result of their simple synthesis route and the use of CO₂ [24]. For example, solvent systems containing ethylene carbonate or glycerol carbonate have been tested in an effective lignocellulosic biomass pre-treatment [35]. In addition, propylene carbonate and glycerol carbonate have been presented as greener substitutes for aprotic highly dipolar and polar aprotic solvents,

respectively, because of their different behavior as a consequence of their different functional groups [36]. Scarce examples can be found in the literature regarding the use of propylene carbonate to separate key mixtures in the chemical industry, standing liquid-liquid extraction processes to separate aromatic/aliphatic mixtures as the most highlighted proposal [37–39]. Nevertheless, there is not available any other cyclic carbonate proposed as separation agent, finding interesting functional groups in the literature that can be successfully tuned for specific tasks [24].

Our research group has developed a multiscale computational strategy, which integrates molecular and process evaluation, to design new solvents and evaluate their performance in industrial separation processes [40]. This methodology was successfully applied to other separations [41,42] or aromatic/aliphatic separations [43–45], among others. First, molecular simulations using COSMO-RS method allow evaluating and selecting the solvents using thermodynamic criteria as distribution ratio, selectivity, and relative volatility [46]. Then, process simulation using COSMO/Aspen methodology [47] let us evaluate selected solvents at process scale studying both the technical and economic viability of the operation by comparing to available technologies [48]. Pros and current boundaries related to multiscale approaches can be checked at recent reviews [49,50].

This work presents cyclic carbonates as a new class of CO₂-derived solvents with promising properties for aromatic/aliphatic separations. Aiming to cover a wide range of possibilities, seven representative cyclic carbonates [(chloromethyl)ethylene carbonate, styrene carbonate, butylene carbonate, cyclohexene carbonate, glycerol carbonate, hexylene carbonate and propylene carbonate] were tested to separate three representative hydrocarbon mixtures [{*n*-heptane + toluene}, {benzene + cyclohexane} and {cyclohexane + cyclohexene}], covering both liquid-liquid extraction and extractive distillation approaches. It is noticeable that some functionalization may impose a less sustainability to the proposal, such as chloride-based solvents; however, the purpose of the selection is identifying property-structure relationship for frequently used cyclic carbonates rather than narrowing down species prior to their evaluation as solvent by sustainable issues.

Results were systematically compared to those obtained by using sulfolane and *N*-formylmorpholine (NFM), as benchmark industrial extractive solvents [47]. The first part of the work is devoted to applying COSMO-RS method to characterize the thermodynamic properties of pure, binary, and ternary mixtures of carbonate/aromatic or alkene/aliphatic compounds. The second part of the proposal involves the phase equilibria prediction and the evaluation of separation properties, namely extractive properties -distribution ratio and selectivity- and relative volatility, by using COSMO-based/Aspen approach. Finally, new separation processes based on liquid-liquid extraction and extractive distillation using cyclic carbonates as solvents were modeled by Aspen Plus simulation, in order to analyze their performance in aromatic-aliphatic separation at process scale. For comparison purposes, process simulations at given operating conditions were done using benchmark industrial solvents, sulfolane and *N*-formylmorpholine (NFM) [51]. Final remarks on recoveries, purities and energy consumption are given to guide the promising use of cyclic carbonates in aromatic-aliphatic separation by liquid-liquid extraction or extractive distillation at commercial standards.

2. Computational details

2.1. Molecular simulations

The electronic structures for the seven cyclic carbonates depicted in Table 1 were calculated using the software Turbomole 4.4.1 and its graphical interface TmoleX [47]. Geometries were optimized at BP86/TZVP quantum chemical level, using the COSMO continuum solvation method [52]. Vibrational frequency calculations were made to ensure that the optimized molecular structures present the minimum level of

Table 1
Cyclic carbonates names, abbreviations, and chemical structures.

Compound	Alias	Structure
(Chloromethyl)ethylene carbonate	Chl-C	
Styrene carbonate	Sty-C	
Butylene carbonate	But-C	
Cyclohexene carbonate	Cyc-C	
Glycerol carbonate	Gly-C	
Hexylene carbonate	Hex-C	
Propylene carbonate	Pro-C	

energy. COSMO files needed to perform COSMO-RS calculations were also obtained from Turbomole using COSMO continuum solvation method for each cyclic carbonate. In order to perform COSMO-RS [53] calculations, the program COSMOtherm version 19.0.4 [54] was used, selecting its implicit BP_TZVP_19 parametrization. First, the main pure properties of the carbonates were calculated (molecular weight, density, boiling point, vapor pressure and viscosity). Additionally, histograms that represent the polarized charge distribution on the electronic surface of the molecular structures (σ -profile) were obtained, which provide abundant information about the molecular nature. The thermodynamic behavior of the binary mixtures between selected carbonate solvents and hydrocarbon compounds was analyzed by means of the activity coefficients at infinite dilution (γ^∞) of hydrocarbon compounds in carbonate solvents, as reference interaction parameter independent of the mixture composition. This parameter is related to the main indicators of separation effectiveness in liquid-liquid extraction, namely the distribution ratio of aromatic compound (2) between immiscible liquid phases ($K_{D,2}$; Eq. (1)) and the aromatic/aliphatic selectivity ($S_{2,1}$; Eq. (2)):

$$K_{D,2} = \frac{x_2^E}{x_2^R} = \frac{\gamma_2^R}{\gamma_2^E} \quad (1)$$

$$S_{2,1} = \frac{K_{D,2}}{K_{D,1}} = \frac{\gamma_2^R}{\gamma_1^R} \cdot \frac{\gamma_1^E}{\gamma_2^E} = \frac{\gamma_1^E}{\gamma_2^E} \cdot \frac{\gamma_2^R}{\gamma_1^R} \quad (2)$$

where x_i^E and x_i^R are the molar fractions of aromatic/alkene compound (2) or aliphatic compound (1) in the extract (E) and raffinate (R) liquid phases, respectively, and γ_i^E and γ_i^R refers to the activity coefficient of aromatic/alkene (2) and aliphatic (1) compounds in the extract and raffinate, respectively.

Regarding extractive distillation, the main thermodynamic parameter of reference for separation effectiveness is the aliphatic/aromatic relative volatility ($\alpha_{1,2}$; Eq. (3)):

$$\alpha_{1,2} = \frac{\frac{\gamma_1 P_1^*}{\varphi_1}}{\frac{\gamma_2 P_2^*}{\varphi_2}} = \frac{\gamma_1}{\gamma_2} \cdot \frac{P_1^* \varphi_2}{P_2^* \varphi_1} \quad (3)$$

where $\gamma_{i,j}$ refers to the activity coefficient of aromatic/alkene (2) and aliphatic (1) compounds in the liquid phase, respectively, P_i^* refers to the saturated vapor pressure of the pure compounds 1 or 2, and $\varphi_{i,j}$ is the fugacity coefficient of compounds 1 or 2.

In addition, excess properties such as excess enthalpy (H^E) and excess entropy ($-TS^E$) for equimolar binary mixtures were calculated by COSMO-RS, since these thermodynamic parameters have been successfully applied for the design of new solvents in separation processes [41]. Experimental values [55–60] for excess enthalpies and activity coefficients at infinite dilution between hydrocarbons and similar carbonates to the ones employed in this work were collected and compared to the analogous values obtained using COSMO-RS calculations. These comparisons can be found in Figs. S1 and S2 in Supplementary material.

2.2. Phase equilibria predictions

The carbonates involved in this work were included in Aspen Plus v.11 simulator following the COSMO-based/Aspen methodology described elsewhere [41,42,47], since these compounds were not available on Aspen Plus databanks. The parameters needed to completely define the pseudo-components and the property package were calculated using COSMOtherm version 19.0.4. COSMO-SAC property model developed by Lin and Sandler [61] was used to estimate the activity coefficients of the mixtures. This methodology has been validated in previous publications for aliphatic/aromatic separations using ILs [7,43,44,48].

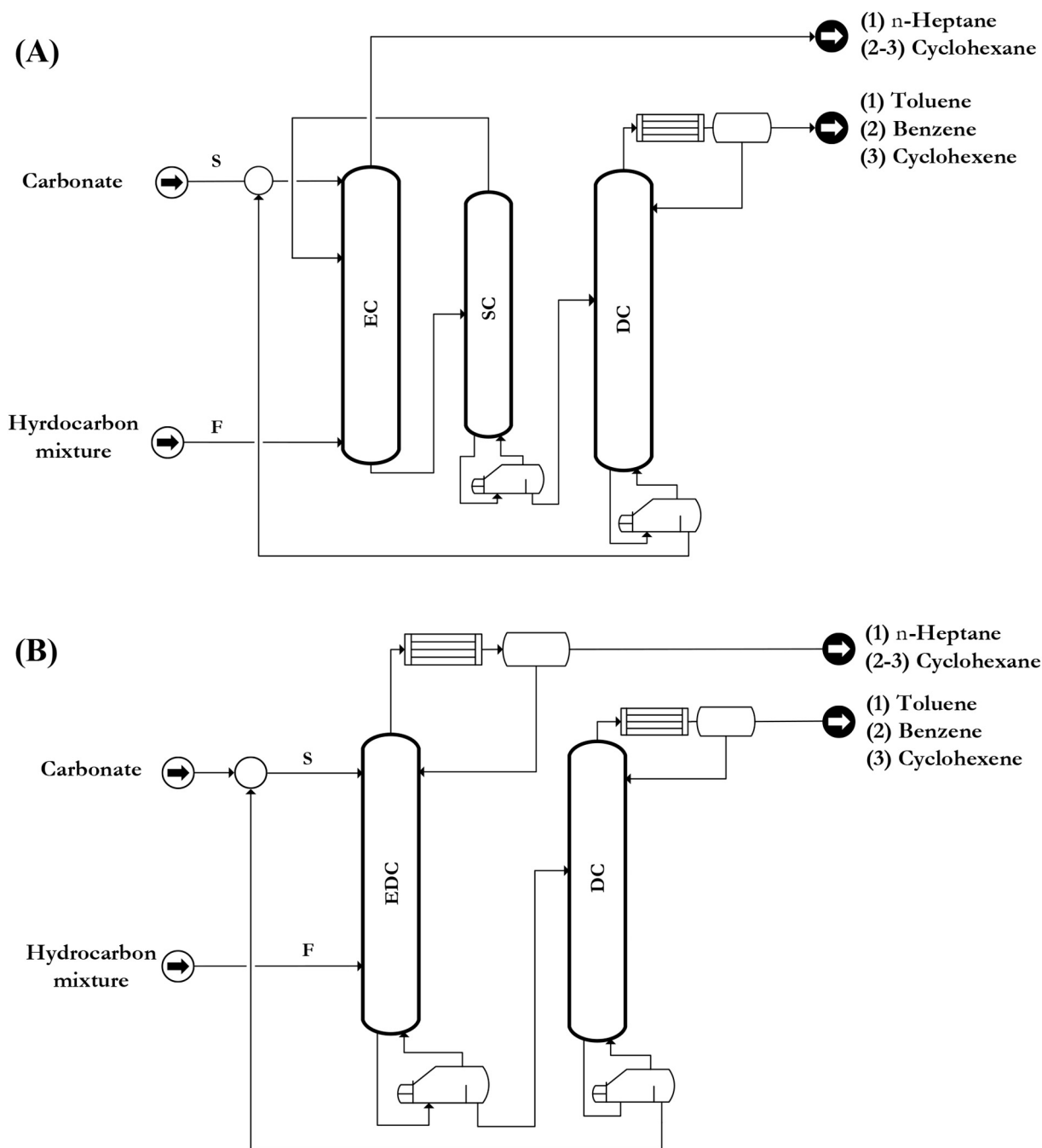
Regarding phase equilibria predictions, liquid-liquid ternary diagrams were calculated for all the mixtures involved in the work by COSMO-based/Aspen approach using Ternary Diagram tool from Aspen Properties calculations. Equilibrium data predictions were compared with the available data reported on the literature, in order to validate the selected thermodynamic model [37,38,62,63]. From liquid-liquid equilibrium data, extractive properties were calculated and evaluated within the whole hydrocarbons compositions and compared with a relevant conventional solvent (sulfolane). In addition, a flash unit was used to calculate the relative volatility of the hydrocarbon mixtures in presence of the different carbonates. Hydrocarbon mixtures with diverse aromatic/aliphatic content were fed to the unit, at the same time the carbonate feed was modified to have a S/F ratio of 1 or 5, and the results were compared with the ones obtained with the benchmark solvent (NFM).

2.3. Process simulation

The final schemes built to model the liquid-liquid extraction (LLE) and extractive distillation (ED) processes are shown in Scheme 1. Process simulation specifications are summarized on Table S1 from Supplementary material. There are three different process schemes depending on the analysis, two of them are used for solvent screening stage and defining commercial specifications in liquid-liquid extraction (shown in Fig. S3 from Supplementary material and Scheme 1A, respectively), while the other one comprises both solvent screening and commercial specifications for extractive distillation (Scheme 1B). Cases labeled as 1 display a comparison between the different carbonates and the conventional solvents (sulfolane and NFM) at benchmark specifications noted below, whereas cases marked as 2 indicate further simulations with the best cyclic carbonate and the conventional solvent to meet commercial purities and recoveries.

2.3.1. Case LLE1

This case comprises the solvent comparison in the open liquid-liquid extraction process (Fig. S3 from Supplementary material). Extraction



Scheme 1. Conceptual diagram of the liquid-liquid extraction process (A) and the extractive distillation process (B) for the separation of the three hydrocarbon systems {*n*-heptane + toluene} (1), {cyclohexane + benzene} (2), {cyclohexane + cyclohexene} (3), as feed (F), using carbonates as solvents (S).

column (EC) works at reference conditions, S/F ratio of 5 and 15 stages (see Table S1 from Supplementary material) [7], collecting the aliphatic (*n*-heptane or cyclohexane) as raffinate and the solvent together with the aromatic/alkene as extract stream. Because of the wide differences in aromatic/alkane purity and recovery, the separation train was designed *ad hoc* for each solvent, only maintaining the number of stages between solvents.

The stripping column (SC) purifies the extract stream, fixing an aromatic/alkene purity specification of 99% in the residue stream with respect to the hydrocarbon fraction, being the adjusted variable the reboiler's duty. The distillation column (DC) allows regenerating the carbonate solvent and obtaining the aromatic/alkene product (toluene, benzene, or cyclohexene, in each case) adjusting the reboiler's duty and the distillate rate to achieve a purity of 99% in each particular case.

2.3.2. Case LLE2

In this case (Scheme 1A), only the selected carbonate and sulfolane are tested in a close-cycle liquid-liquid extraction process. This case specifies commercial recovery (99.9%) and purity (99.9 wt%) of aromatic/alkene in the process. In addition to the procedure described in Case LLE1, aromatic/alkene recovery is addressed by properly adjusting solvent consumption, whereas aromatic/alkene purity was achieved following the same procedure described in Case LLE1.

2.3.3. Case ED1

In the extractive distillation process the solvents' performance is compared (Scheme 1B) at the same specifications (the same equipment conditions—see Table S1 from Supplementary material for details-). The extractive distillation column (EDC) is designed at reference conditions

to evaluate both hydrocarbons' recoveries and purities, fixing S/F ratio of 5 and 15 stages as *Case ELL1* [7]. The distillation column (DC) was designed to fully separate the toluene, benzene or cyclohexene from the carbonate, which is recirculated back to the extractive distillation column. It is relevant to underline that both columns work specifying an ideal distillate rate of 500 kg/h, which envisions the utopic complete separation. This particular selection means that the values of hydrocarbons' recoveries and purities are equal.

2.3.4. Case ED2

In this case, only the most competitive carbonate and NFM are selected and tested against each other. The procedure aims to obtain a 99.9 wt% of aromatic or olefin purity and 99.9% of aromatic or olefin recovery.

Extraction column (EC) was modeled by EXTRACT module, whereas distillation (DC), extractive distillation (EDC) and stripping columns (SC) were modeled by RADFRAC model, in equilibrium mode, as implicit in Aspen Plus v.11. Recoveries, purities, and energy demand per kg of recovered aromatic/alkene product (MJ/kg) were used to evaluate solvent performance in both separation processes at industrial scale. The last one is an essential parameter to keep in mind the design of less energy demanding processes rather than slightly reducing investment cost by selecting solvents with better separation parameters [64]. In this way, also solvent losses are monitored when selecting the solvent, since emissions are reducing separation steps remain essential tasks, as exemplified for non-volatile solvents [65].

3. Results

3.1. COSMO-RS analysis of pure cyclic carbonates: properties and potential compound interactions

COSMO-RS method was applied to predict relevant physicochemical properties of the seven cyclic carbonates, to be used as extracting or entrainer solvents (Table 2). As can be seen, in the case of the studied carbonates, COSMO-RS predictions give reasonable results of pure compound properties. The molecular weights and boiling points are in general in the range of NFM and sulfolane, and some carbonates even present higher boiling points, which would be translated into lower solvent losses in distillation stages. The densities of the carbonates are, in general, similar, or higher than NFM's and sulfolane's densities, except for Hex-C. In addition, some carbonates present lower (Pro-C, But-C) or similar (Hex-C, Cyc-C) viscosities than the benchmark solvents, whereas others are significantly more viscous (Gly-C, Sty-C).

COSMO-RS provides the σ -profile of the studied cyclic carbonates, which can be used to anticipate their behavior in aromatic-aliphatic separations [46]. First, propylene carbonate (Pro-C) is used as reference and its σ -profile is compared with those of toluene and *n*-heptane (Fig. 1). Pro-C presents a peak around $\sigma \approx 0.01 \text{ e}/\text{\AA}^2$ due to the presence of the polar carbonyl group, revealing its hydrogen bond acceptor character. Attending to the charge distribution in the non-polar region

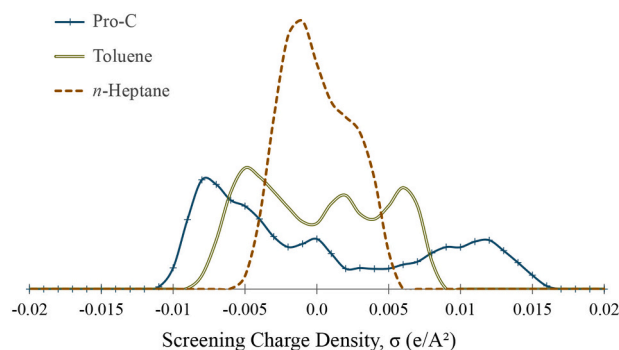


Fig. 1. σ -Profile of propylene carbonate (Pro-C), toluene and *n*-heptane.

($-0.0082 \text{ e}/\text{\AA}^2 < \sigma < 0.0082 \text{ e}/\text{\AA}^2$), it is evident that Pro-C presents higher similarity with toluene (peaks located at $-0.0082 \text{ e}/\text{\AA}^2 < \sigma < -0.025 \text{ e}/\text{\AA}^2$ and $0.025 \text{ e}/\text{\AA}^2 < \sigma < 0.0082 \text{ e}/\text{\AA}^2$) than with *n*-heptane (Pro-C does not show a peak centered on $\sigma \approx 0 \text{ e}/\text{\AA}^2$, corresponding to aliphatic groups). Therefore, COSMO-RS description of pure compounds anticipates a greater affinity between toluene and carbonate compounds than with *n*-heptane.

The presence of different functional groups in the remaining carbonates significantly changes their σ -profile (Fig. S4 from Supplementary material), suggesting a range of different behaviors as solvents. All the carbonates present hydrogen bond acceptor capacity due to the carbonyl group ($\sigma \approx 0.01 \text{ e}/\text{\AA}^2$). However, the presence of chloride and hydroxyl functional groups in, respectively, Chl-C and Gly-C compounds confers hydrogen bond donor character (peaks in the region $\sigma < -0.0082 \text{ e}/\text{\AA}^2$), increasing the polarity of the carbonate solvent. In contrast, carbonates with longer alkyl chain (But-C, Cyc-C and Hex-C) present increasing contribution of electronic density centered on $\sigma \approx 0.01 \text{ e}/\text{\AA}^2$, revealing a higher non-polar character. On the other hand, adding benzene group (Sty-C) contributes to the aromaticity of the carbonate compound.

In conclusion, the different functional groups of the carbonates contribute to emphasize their polar or non-polar character, which may translate into a higher or lower affinity for the aromatic or aliphatic compounds.

3.2. Solute-solvent interactions: analyzing the carbonate-hydrocarbon binary mixtures to draft the separation behavior

COSMO-RS is now used to analyze the thermodynamic behavior of {hydrocarbon + carbonate} binary systems. First, activity coefficients at infinite dilution predicted using COSMO-RS data were compared with the corresponding literature data, finding a tight correlation between them, even involving the effect of temperature, as can be seen in Fig. S1 in Supplementary material. Then, the same method was followed with the excess enthalpies of hydrocarbon-carbonate mixtures finding that the interaction energy predictions follow the same

Table 2

Cyclic carbonates main pure properties calculated using COSMO-RS. Values in brackets are from literature.

Carbonate	Molecular weight (g/mol)	Density at 293–298 K (g/ml)	Normal boiling point (K)	Vapor pressure at 293–298 K (Pa)	Viscosity at 293–298 K (cP)	Ref.
Chl-C	136.53	1.52	647	0.04	8.1	
Sty-C	164.16	1.30	675	0.02	14.3	
But-C	116.12	1.18 (1.14)	570 (524)	2.59 (3.73)	2.5 (3.2)	[66]
Cyc-C	142.15	1.25	627	0.34	3.8	
Gly-C	118.09	1.45 (1.40)	588 (512)	0.14 (0.93)	46.0 (85.0)	[67]
Hex-C	144.17	1.09	595 (535)	0.59	3.7	[68]
Pro-C	102.09	1.26 (1.20)	571 (515)	2.85 (3.0)	2.3 (2.5)	[66]
NFM	115.13	1.18 (1.14)	535 (513)	9.28 (3.0)	3.3 (7.66)	[69]
Sulfolane ^a	120.17	1.31 (1.26)	616 (560)	0.66 (9.1)	3.28 (10.5)	[70]

^a Sulfolane's density, vapor pressure and viscosity values presented correspond to 303 K due to its higher melting point.

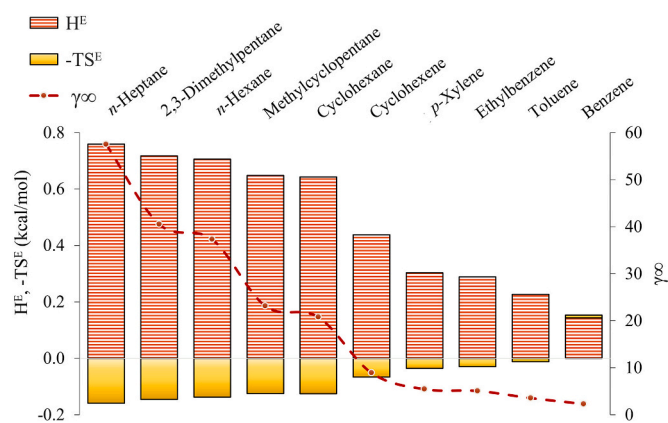


Fig. 2. Activity coefficients at infinite dilution of hydrocarbons in propylene carbonate and excess enthalpies and entropies of hydrocarbon + propylene carbonate equimolar mixture at 298 K.

qualitative tendency as the experimental data, as can be seen in Fig. S2 in Supplementary material. Afterwards, the carbonates and hydrocarbons selected for this work were studied. Fig. 2 shows the calculated activity coefficients at infinite dilution of different hydrocarbons (alkanes, alkenes, and aromatics) in Pro-C solvent (γ^∞) and the excess enthalpy and excess entropy (H^E and $-TS^E$) of {hydrocarbon + Pro-C} equimolar binary mixtures. As can be seen, there is a wide range of mixing behaviors, with activity coefficient values evolving from ~ 1 (remarkable case: benzene; nearly ideal behavior; expected high solute solubility in carbonate) to 60 (case of reference: *n*-heptane, strong positive deviation from Raoult's law; possible presence of two immiscible liquid phases). As shown in Fig. 2, the thermodynamics of {hydrocarbon + carbonate} mixtures are governed by the enthalpy, finding in all cases endothermic mixtures, where the increment of entropy imposes a minor role. The mixtures of hydrocarbons with carbonate solvents are less favorable (higher γ^∞ values) in aliphatic compounds with respect to aromatic ones. Increasing the C number of hydrocarbons or cyclic structures also implies lower affinity (higher γ^∞ values) towards carbonate compound (Fig. 2). These trends are in good agreement with those discussed in the literature for other solvents [71], suggesting the suitability of using cyclic carbonates for aromatic/aliphatic separation. COSMO-RS results of the rest of {hydrocarbon + carbonate} mixtures can be found in Tables S2-S4 of the Supplementary material, achieving nearly the same conclusions.

Next step is to analyze the role of solvent structure in the behavior of {hydrocarbon + carbonate} mixtures. Fig. 3A compares the γ^∞

values of *n*-heptane and toluene in the different carbonates. It seems evident that all studied solvents interact more favorably with toluene, as solute, than with *n*-heptane, which may present immiscibility with the solvents due to the high γ^∞ values. The different functional groups in the cyclic carbonate strongly influence its interaction with *n*-heptane solute, with activity coefficients of the aliphatic ranging from > 420 (in the more polar solvents: Chl-C or Gly-C) to < 10 (in carbonates with remarkably non-polar character: Hex-C, Cyc-C). On the other hand, the γ^∞ values of the interaction with toluene (Fig. 3A) follow nearly the same trend than that of *n*-heptane, but with tighter value range: from 14.0 to 1.5.

Since the extractive properties of the solvent (distribution ratio and selectivity in Eqs. (1) and (2), respectively) are determined by the activity coefficients of hydrocarbons in the mixture, Fig. 3A can be used to anticipate the performance of carbonate compounds as extractive agents. In this sense, distribution ratio ($K_{D,2}$) of the aromatic compound between carbonate-rich phase and an aliphatic rich-phase can be expected to follow the same trend than $1/\gamma_2^\infty$ (Eq. (1)). Following the same reasoning, aromatic/aliphatic selectivity ($S_{2,1}$, Eq. (2)) and aliphatic/aromatic relative volatility ($\alpha_{1,2}$, Eq. (3)) would be proportional to the activity coefficient ratio ($\gamma_1^\infty/\gamma_2^\infty$). The low γ^∞ values of toluene in the non-polar carbonates (Cyc-C and Hex-C) anticipate a high distribution ratio in LLE ternary systems, whereas their low *n*-heptane/toluene activity coefficient ratio ($\gamma_1^\infty/\gamma_2^\infty$ in Fig. 3A) indicates low aromatic/aliphatic selectivity; in fact, these carbonates seem to present similar mixture behavior than the industrial benchmark solvent NFM. In contrast, those carbonates with higher polar character (Chl-C and Gly-C) are expected to present high aromatic/aliphatic selectivity but very low extraction capacity for aromatics. Carbonate solvents with intermediate polarity (Pro-C, But-C, Sty-C) show a midway thermodynamic behavior, close to that of benchmark industrial solvent sulfolane.

Regarding extractive distillation, its main performance indicator is the aliphatic/aromatic relative volatility ($\alpha_{1,2}$), which, as mentioned above, is related to $\gamma_1^\infty/\gamma_2^\infty$ ratio by Eq. (3). Attending to results in Fig. 3A, polar carbonates (Chl-C and Gly-C) would promote the volatility of aliphatics from aromatics; however, the high activity coefficient values prevent of obtaining required solubility of hydrocarbons in the ternary mixture. Nevertheless, low ($\alpha_{1,2}$) values with high solubility are implied for non-polar carbonates (Cyc-C and Hex-C), which are close to NFM's values. Finally, intermediate carbonates (Pro-C, But-C) may be competitive as entrainers in the hydrocarbon separation by extractive distillation with moderate solvent consumption.

Then, the possible application of the carbonates in the separation of the three representative hydrocarbon mixtures, namely {*n*-heptane + toluene}, {benzene + cyclohexane} and {cyclohexane + cyclohexene}, was

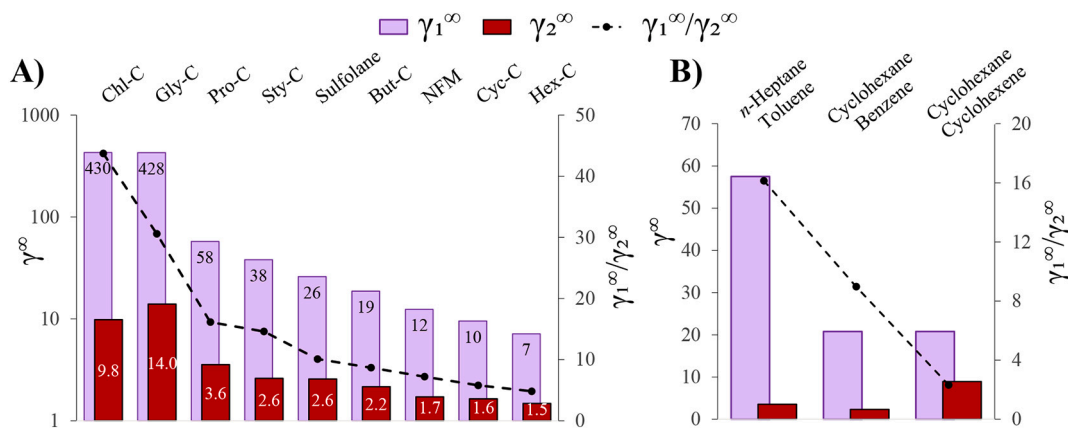


Fig. 3. A) Activity coefficients at infinite dilution (left axis, in logarithmic scale) of *n*-heptane (1) and toluene (2) in cyclic carbonates and conventional solvents. *n*-Heptane (1) / toluene (2) activity coefficient ratio (right axis). B) Activity coefficients at infinite dilution and activity coefficient ratios for {*n*-heptane (1) + toluene (2)}, {cyclohexane (1) + benzene (2)} and {cyclohexane (1) + cyclohexene (2)} mixtures in propylene carbonate (Pro-C).

analyzed. Fig. 3B compares the activity coefficient at infinite dilution of the different hydrocarbons and their corresponding ratios in propylene carbonate (Pro-C), used as benchmark. As can be seen, all mixtures show more favorable interaction between the carbonate and the aromatic or alkene than between the carbonate and the aliphatic, with $\gamma_1^\infty/\gamma_2^\infty$ values always greater than 1, implying that the three mixtures are suitable for separation using carbonate solvents. As expected, COSMO-RS also indicates that {*n*-heptane + toluene} system will present the most favorable separation attending to the highest aliphatic (1) / aromatic (2) $\gamma_1^\infty/\gamma_2^\infty$ ratio, followed by {cyclohexane + benzene} system and then {cyclohexane + cyclohexene}. Similar results are found for the rest of the carbonates, which can be seen in Table S5 in the Supplementary material.

3.3. Phase equilibria for ternary systems: envisioning separation conceptual designs from extractive properties and relative volatilities

Following, the phase equilibrium data for {aromatic/alkene + aliphatic + carbonate}, ternary systems predicted by COSMO-based/Aspen approach are analyzed. First, the computational method was successfully validated using the scarce but representative experimental data from the literature, as can be seen in Fig. S5 in the Supplementary material. Fig. 4 shows representative liquid-liquid ternary-like diagrams (mass fraction) for the {*n*-heptane + toluene} separation case using cyclic carbonates. As seen, the behavior of carbonates ranges from high toluene solubility and low toluene/*n*-heptane selectivity (Hex-C) to high toluene/*n*-heptane selectivity and low toluene solubility (Chl-C). There are also intermediate cases, such as But-C solvent, as can be seen in Fig. S6 of the Supplementary material, together with the ternary diagrams of the rest of carbonates. These data are in good agreement with conclusions extracted from the previous study, concluding that the polarity of the carbonate structures determines their extractive properties.

For further inspecting the behavior of studied cyclic carbonates as extracting solvent, Fig. 5 presents the toluene (2) / *n*-heptane (1) selectivity ($S_{2,1}$) and toluene (2) distribution ratio ($K_{D,2}$) (in mass units) in a complete range of compositions (mass fraction), estimated by Eqs. (1) and (2) from LLE data predicted by COSMO-based/Aspen methodology. In agreement with above results, the $K_{D,2}$ parameters decreases with the polarity of carbonate solvent in the order Hex-C \approx Cyc-C > But-C > Prop-C > Sty-C > Gly-C \approx Chl-C (Fig. 5A). Aromatic distribution ratio remains nearly constant for a wide range of mixture compositions, but slightly increases at high toluene mass fraction for less polar carbonates. It should be emphasized that sulfolane benchmark solvent presents intermediate $K_{D,2}$ values respect to studied sample of carbonate solvents. Regarding the toluene/*n*-heptane selectivity ($S_{2,1}$) (in mass units), an opposite tendency is observed (Fig. 5B). Moreover, selectivity is notably affected by mixture composition, significantly

decreasing with toluene mass fraction, especially for polar carbonates (Chl-C). An interesting fact is that the available liquid-liquid equilibrium range drastically increases from least polar carbonate (Hex-C) towards most polar one (Chl-C), which constrains their application in considered separation processes, pointing intermediate polar carbonates as the most suitable. For the other two systems, reference ternary diagrams with propylene carbonate can be found in Fig. S7 in Supplementary material.

Fig. 5C compares the values of aromatic distribution ratio and aromatic/aliphatic selectivity of {*n*-heptane + toluene} for the selected cyclic carbonates and sulfolane at given aromatic mass fraction in raffinate phase. Clearly, cyclic carbonates present a wide range of behavior as extractive agents. One the one hand, there are polar carbonates with high selectivity but low partition coefficient (Chl-C and Gly-C) compared with sulfolane; on the other hand, those carbonates functionalized with long alkyl groups (Hex-C and Cyc-C) present the opposite properties. Furthermore, there is a group of carbonates (Sty-C, Pro-C and But-C) with similar properties to sulfolane's, portraying them as tempting alternatives. It should be noted that non-polar carbonates (Hex-C and Cyc-C) with low liquid-liquid equilibrium range could not be applied to treat current BTX sources (Fig. 5D), but Sty-C, Pro-C and But-C still present similar properties to sulfolane in those conditions.

Then, the relative volatilities ($\alpha_{1,2}$) of *n*-heptane (1) from toluene (2) in presence of cyclic carbonates are predicted by COSMO-based/Aspen approach, in order to evaluate their application as entrainers in extractive distillation for aromatic/aliphatic separations. Fig. 6A depicts the calculated $\alpha_{1,2}$ values (mass units) of the different solvents as function of the hydrocarbon mixture composition feed. First, it should be noted that some carbonates -those intermediate in polarity-, namely But-C, Pro-C and Sty-C, exhibit an alteration in the aliphatic/aromatic relative volatility trend, with an abrupt slope change at some toluene compositions, as a consequence of the disappearance of one of the two immiscible liquid phases, evolving from a vapor-liquid-liquid equilibrium (VLLE) to a vapor-liquid equilibrium (VLE). In contrast, the polar carbonates (Chl-C and Gly-C) present a VLLE equilibrium for all toluene compositions, while the non-polar carbonates (Hex-C and Cyc-C) only exhibit VLE. It should be emphasized that the presence of biphasic liquid mixtures implies higher technical complexity to design and operate an extractive distillation column. At low aromatic composition (where most systems present VLLE), the solubility of solutes in the mixture seems to play the key role, thus providing Cyc-C and Hex-C the best performance, with values in the range of those of NFM. In contrast, at high toluene mass fraction (where ternary systems present VLE, with the exception of Chl-C and Gly-C), the aliphatic/aromatic relative volatility follows the trend of aromatic/aliphatic selectivity, revealing Pro-C and Sty-C as promising entrainer candidates compared to industrial solvent NFM. We should note that the carbonate composition in

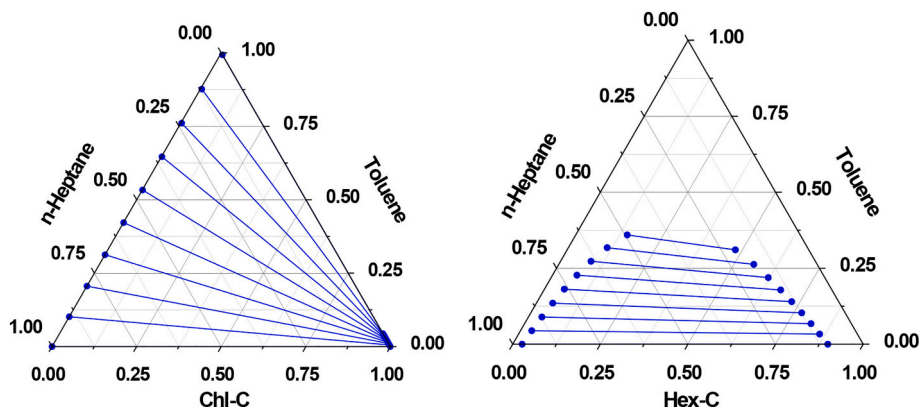


Fig. 4. Liquid-liquid ternary diagrams (mass fraction) for representative cases of {toluene + *n*-heptane + carbonate} mixtures predicted by COSMO-based/Aspen approach.

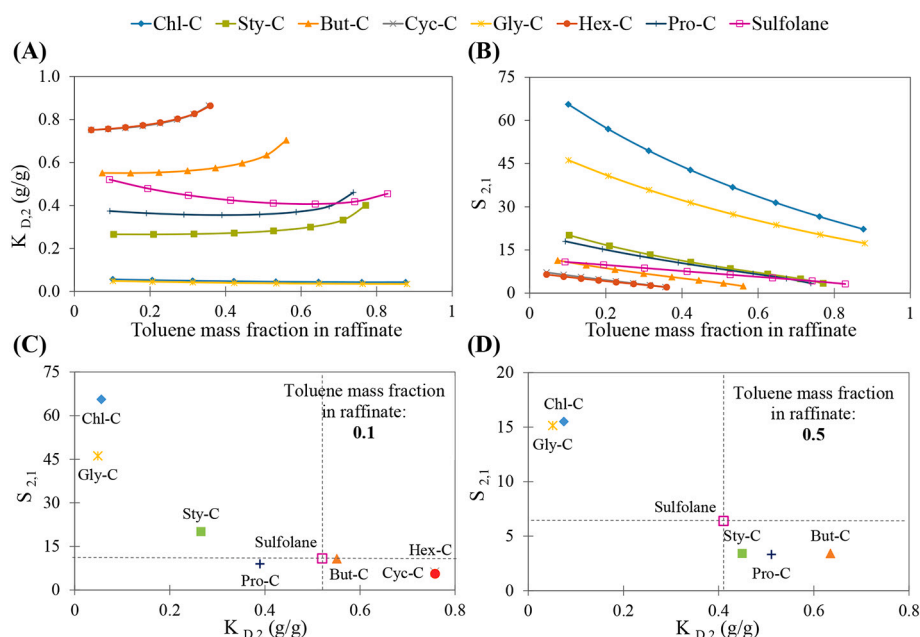


Fig. 5. Extractive properties (mass units) of carbonates and benchmark conventional solvents in the whole range of hydrocarbon compositions. (A) toluene mass distribution ratio; (B) toluene/*n*-heptane selectivity; (C) toluene/*n*-heptane selectivity vs toluene mass distribution ratio for a toluene mass fraction of 0.1 in raffinate; (D) toluene/*n*-heptane selectivity and toluene mass distribution ratio for a toluene mass fraction of 0.5 in raffinate.

the ternary mixture also has a main influence on $\alpha_{1,2}$ values (Fig. 6B), generally increasing the aliphatic/aromatic relative volatility with S/F ratio; in addition, depending on solvent consumption, other cyclic carbonates (as But-C for S/F = 5) present higher relative volatility than the conventional solvent (NFM). Summarizing, current theoretical results indicate that some carbonates may comprise entrainer properties to be a promising alternative for {*n*-heptane + toluene} separation by extractive distillation, since they present similar or higher relative volatility values than NFM.

Fig. 7 shows the same analysis comparing the three studied systems with propylene carbonate (Pro-C), same data for the remaining carbonates can be found in Figs. S8 and S9 in Supplementary material. The {cyclohexane + benzene} system follows a similar trend to {*n*-heptane + toluene} system regarding liquid-liquid extraction parameters (Fig. 7A); however, Pro-C presents higher extraction capacity for benzene than toluene, but lower selectivity for aromatic respect to cyclohexane than to *n*-heptane. On the other hand, {cyclohexane + cyclohexene + Pro-C} system shows remarkably low partition coefficients and selectivity, due to the lower and higher solubility, respectively, of cyclohexane and cyclohexene in the cyclic carbonate. It reveals the liquid-liquid extraction process as an impractical separation for {cyclohexane + cyclohexene} mixture. Regarding extractive distillation (Fig. 7B), {*n*-heptane + toluene} would represent the most suitable separation by using cyclic carbonates, with the highest values of aliphatic/aromatic relative volatility, followed by {cyclohexane

+ benzene} and, lastly {cyclohexane + cyclohexene}. It is remarkable that the latter system's relative volatility is not affected by cyclohexene feed composition when using propylene carbonate, since the slight difference in structure from cyclohexane to cyclohexene does not lead to impose significant changes in solvent effectiveness, as previously noted elsewhere [9].

3.4. Evaluation of cyclic carbonates at process scale

The impact of cyclic carbonates at both liquid-liquid extraction and extractive distillation processes are discussed in this section. First, {*n*-heptane + toluene} system is used as reference and liquid-liquid extraction process is presented, from screening of carbonates, in order to select the most efficient, to preliminary design at commercial specifications. Second, extractive distillation technology is envisioned as an alternative to liquid-liquid extraction one, following the same methodological structure. Finally, the application of both technologies in the other systems is discussed.

3.4.1. Liquid-liquid extraction for {*n*-heptane + toluene}

At process scale, liquid-liquid extraction process is firstly tested for a toluene and *n*-heptane mixture with 50 wt% of each hydrocarbon. The seven carbonates together with the benchmark solvent (sulfolane) are screened at the typical open process scheme, reported in Fig. S3 in the Supplementary material applying the specifications shown in Table S1

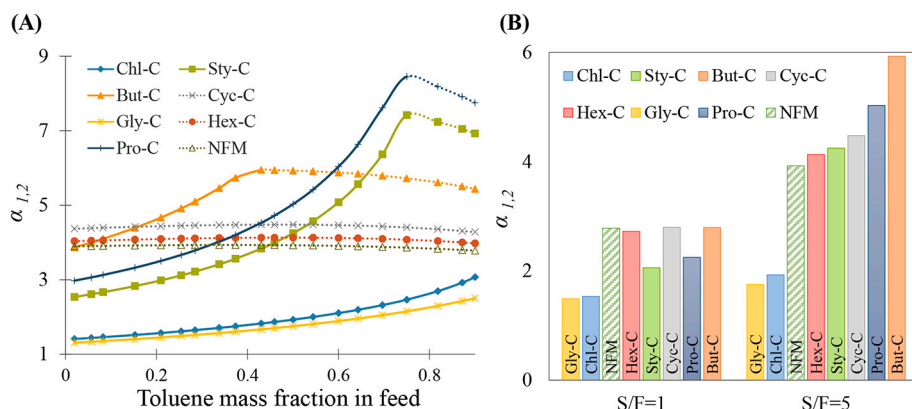


Fig. 6. Relative volatility (mass units) of *n*-heptane from toluene in the presence of cyclic carbonates and N-formylmorpholine (NFM). (A) as a function of toluene composition in feed and S/F = 5 (solid lines denote 2 liquid phases and dotted lines denote 1 liquid phase) and (B) values for a 0.5 mass fraction of toluene in feed for S/F = 1 and S/F = 5.

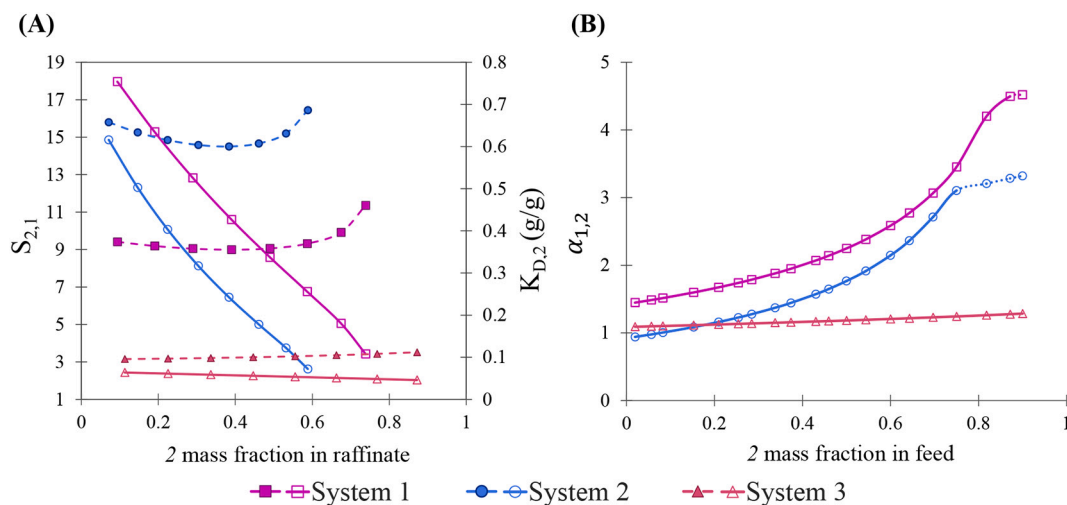


Fig. 7. Liquid-liquid extraction and extractive distillation properties for systems: (1) {n-heptane (1) + toluene (2)}, (2) {cyclohexane (1) + benzene (2)} and (3) {cyclohexane (1) + cyclohexene (2)}; (A): $S_{2,1}$ (solid line) and $K_{D,2}$ (dashed line) as a function of aromatic or olefin composition in raffinate; (B): $\alpha_{1,2}$ in the presence of propylene carbonate with a S/F = 1 as a function of aromatic or olefin composition in feed.

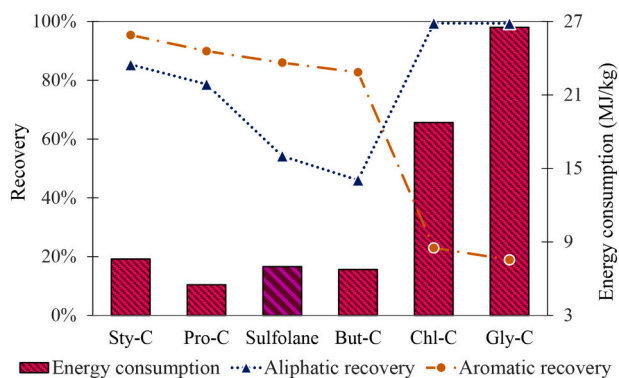


Fig. 8. Aromatic and aliphatic recoveries (wt%) and energy demand in liquid-liquid extraction process for n-heptane/toluene separation using cyclic carbonates and sulfolane.

in Supplementary material, following *Case LLE1* simulations described in “Process simulation” section. The used operating conditions are collected in Table S6 in the Supplementary material. Hydrocarbon recoveries are plotted in Fig. 8 together with specific energy demands for the {toluene + n-heptane} separation. As seen, studied cyclic carbonates exhibit a wide range of solvent performance in process. A carbonate with intermediate extractive properties (Pro-C) allows obtaining higher aromatic and aliphatic recovery with lower energy demand than the benchmark solvent (sulfolane). Other similar carbonates are

competitive in terms of separation (Sty-C) or present close behavior to sulfolane (But-C). Conversely, high selective carbonates (Chl-C, Gly-C) are presenting high energy demands and low recoveries, clearly indicating that the solvent consumption to meet an adequate separation would be unnecessarily high. Finally, high capacity carbonates (Hex-C, Cyc-C) do not provide liquid-liquid phase splitting along the whole composition profile of the extraction column, even at low S/F ratios, revealing its unsuitableness for liquid-liquid separation.

Nonetheless, solvent losses remain essential when dealing with high purity standard separations, still when solvent losses are extremely low, since they can affect the aliphatic purity standard. These values are shown in Table S7 from Supplementary material and permit to conclude that the low solubility in alkanes and the relatively low volatility of cyclic carbonates (Table 2) implies solvent losses in the range or even lower than those obtained for sulfolane solvent.

Then, Pro-C is selected as most promising extracting solvent attending to its favorable separation effectiveness, low energy consumption and high industrial availability [72]. It is compared against sulfolane at process scale for the separation of toluene from n-heptane with a 99.9% aromatic purity and recovery. For this purpose, *Case LLE2* simulations (see “Process simulation” section) were carried out in close cycle process to achieve commercial product standards by tuning the S/F ratio. Table 3 summarizes the extracting solvent performance in terms of specific energy demands, solvent consumption, solvent losses and aliphatic purity and recovery. It is concluded that both solvents present similar behavior in the separation of {n-heptane + toluene}. It should be noted, however, that sulfolane requires lower solvent consumption

Table 3

Solvents and technology comparison regarding solvent losses, specific energy demand and solute purity and recovery (omitted unless lower than 99.9%) for the 2 different technologies (LLE: liquid-liquid extraction; ED: extractive distillation) with different conditions of S/F ratio, reflux ratio (RR) and number of stages, for the three hydrocarbon systems {n-heptane + toluene} (1), {cyclohexane + benzene} (2), {cyclohexane + cyclohexene} (3).

System	Technology	Solvent	Solvent losses (wt%)	Specific energy demand (MJ/kg)	Solute purity (wt%)	Recovery	S/F ratio	RR	Stages
1	LLE	Sulfolane	0.027	3.83			2.5	–	–
	LLE	Pro-C	0.066	3.64	99.6		3	–	–
	ED	NFM	0.370	6.43	99.2	99.2	1	3	40
	ED	Cyc-C	0.007	6.44			1	3	40
2	LLE	Pro-C	0.076	4.04			2.5	–	–
	LLE	Sulfolane	0.026	4.48			2.5	–	–
	ED	NFM	0.153	9.94	99.6		5	3	25
	ED	Cyc-C	0.002	9.97	99.9		5	3	25
3	ED	NFM	0.154	10.93	98.8	99.0	5	4.5	50
	ED	Cyc-C	0.002	10.98	99.0	99.0	5	4.5	50

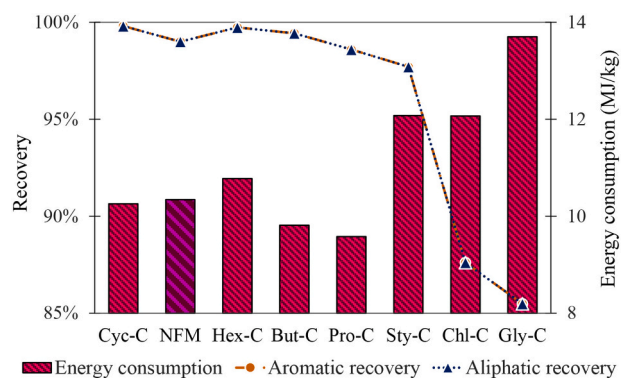


Fig. 9. Aromatic recovery and purity (wt%) and energy demand from extractive distillation process for *n*-heptane/toluene separation using cyclic carbonates and NFM.

and minor solvent losses (which implies slightly higher *n*-heptane purity) than Pro-C. In contrast, the selected carbonate presents slightly lower energy demands, portraying it as an interesting and sustainable alternative for this separation processes.

3.4.2. Extractive distillation for {*n*-heptane + toluene}

The application of cyclic carbonates in extractive distillation for {toluene + *n*-heptane} separation is now evaluated at process scale (Scheme 1B) using Case ED1 simulations described in “Process simulation” section. Fig. 9 compares the process performance of the seven carbonates and NFM (benchmark industrial entrainer), in terms of obtained aromatic recovery and purity and specific energy consumptions. Non-polar carbonates (Cyc-C, Hex-C) stand out as the more efficient mass agents. The high hydrocarbon solubility in Cyc-C and Hex-C is an enhancer aspect in extractive distillation, providing them the best separation performance. On the other hand, But-C and Pro-C (showing high *n*-heptane/toluene relative volatility for S/F = 5 and toluene mass fraction of 0.5, Fig. 6B) stand out as highly efficient solvents, with remarkably low energy consumption compared with NFM; however, they do not enhance the aromatic recovery and purity obtained with the industrial solvent. Lastly, Sty-C, Chl-C and Gly-C (carbonates with polar or aromatic functional groups) present the highest energy consumption and the lowest aromatic recoveries and purities, being disadvantageous alternatives for the separation.

On the other hand, Table S8 from Supplementary material collects solvent losses in distillate streams. As seen, the use of cyclic carbonates imposes a clear advantage when compared to NFM, due the lower volatility of the formers (Table 2).

Summarizing, Cyc-C rendered the most efficient results, with the highest aromatic purity and recovery (99.8%) and lowest solvent losses in these conditions, being the only carbonate able to improve NFM's results, without exceeding its energy consumption. Due to these reasons, it was selected to compare its performance to NFM's at commercial standards, by using Case ED2 simulations described in “Process simulation” section.

Extractive distillation is presented as a more tunable technology than liquid-liquid extraction, since S/F ratio can be decreased to meet the same separation by properly adjusting number of stages and, thus, reducing energy consumption. In Fig. S10 in Supplementary material it is displayed the required number of EDC stages (N) and energy consumption to meet commercial specifications using different S/F ratios, revealing that the specific energy duty can be diminished using lower S/F ratio at the expense of more number of stages. This is an important drawback from liquid-liquid extraction technology when dealing with commercial separations, since the S/F ratio in extractive distillation can even be reduced up to S/F = 1, with a reasonable number of column stages, which implies a drastic decrease in solvent and energy consumption.

Table 3 reports the results in terms of energy demands and equipment requirements fixing the most favorable S/F ratio for each system in terms of energy demand, attempting to design the extractive distillation processes at 99.9 wt% aromatic purity and recovery for {*n*-heptane + toluene}. As can be seen, Cyc-C and NFM show nearly the same entrainer performance in terms energy consumption, solvent use, reflux ratio and number of stages. However, it is not possible to achieve more than 99.2 wt% of toluene purity for NFM, due to its higher volatility compared with Cyc-C (Table 2). Therefore, the use of Cyc-C as solvent in an extractive distillation scheme envisions a promising proposal to separate hydrocarbons, even fulfilling high purity standards.

3.4.3. Process performance of cyclic carbonates for {cyclohexane + benzene} and {cyclohexane + cyclohexene} separation

Process simulation analysis by COSMO-based/Aspen approach was also performed for {cyclohexane + benzene} and {cyclohexane + cyclohexene} separation by liquid-liquid extraction and extractive distillation using cyclic carbonates and benchmark industrial solvents. Screening results for both technologies can be found in Figs. S11–S13 and Tables S7–S8 in Supplementary material. The solvents that could not fulfill the required specifications are not included in those results. In relation to liquid-liquid extraction, benzene is removed efficiently from cyclohexane using carbonate solvents, but the purity of aromatic product is generally lower than in {*n*-heptane + toluene} system, because of the aforementioned cyclohexane higher solubility in carbonate than *n*-heptane. Pro-C was again selected as most promising solvent compared with sulfolane fulfilling commercial standards, i.e. 99.9 wt% purity and recovery of the aromatic or alkene product (Table 3). Comparing to {*n*-heptane + toluene} separation (Table 3), it is observed that {cyclohexane + benzene} requires higher specific energy demand and presents higher solvent losses, due to the more volatile character of this mixture. Nevertheless, Pro-C is found as a promising good alternative to sulfolane, with slightly higher solvent losses but lower energy consumption.

Lastly, the separation of {cyclohexane + cyclohexene} system in liquid-liquid extraction was not successively achieved by using cyclic carbonates; in this sense, in the literature it cannot be found a solvent with extractive properties enough to assay designing an efficient process to separate cyclohexane and cyclohexene by liquid-liquid extraction [9].

Regarding extractive distillation technology, the trends slightly tend to separate carbonates in a wider spectrum, as can be seen in Figs. S12 and S13 in Supplementary material. Focusing on {benzene + cyclohexane}, it is found that Cyc-C > Hex-C > But-C stand out as better mass agents than NFM. Concerning {benzene + cyclohexane}, Cyc-C and Hex-C show better separation values than those for NFM. Energy demand follows the same picture in the two mixtures as that provided for {*n*-heptane + toluene} case, revealing itself almost independent from the mixture nature. Cyc-C was selected again to be compared with NFM using commercial standards for both mixtures. Table 3 reports the results in terms of energy demand and equipment requirements fixing the most favorable S/F ratio for each system, designing the processes at 99.9 wt% in the {cyclohexane + benzene} mixture, whereas {cyclohexane + cyclohexene} separation is addressed at 99.0 wt% of purity. The results portray Cyc-C as an excellent alternative to NFM for both mixtures, with higher purities, same solvent consumption, and similar energy demands. Therefore, the use of Cyc-C as solvent in an extractive distillation scheme envisions a potential proposal to separate hydrocarbons, even fulfilling high purity standards in challenging separations of the chemical industry.

3.4.4. Separation technologies comparison

Last, in order to compare liquid-liquid extraction and extractive distillation processes, Table 3 summarizes the most appropriate technology and solvent for each mixture. The specific energy consumption using Cyc-C and Pro-C for {*n*-heptane + toluene} separation (with

purity standard) was 6.44 and 3.64 MJ/kg for extractive distillation and liquid-liquid extraction, respectively; becoming extractive distillation the most attractive technology for the separation of said mixture in terms of energy demands. Nevertheless, extractive distillation could operate at lower S/F ratios than liquid-liquid extraction, what would mean lower equipment investments; therefore, further cost estimations should be done to decide between technologies. In any case, the computational results reveal more favorable scenarios using cyclic carbonates than those achieved with ionic liquids or eutectic solvents in the recent literature [6,7], and suggests novel processes at low aromatic contents, commented above, where current and new generation solvents are not capable to provide a feasible technology.

On the other hand, when analyzing {benzene + cyclohexane} mixture, differences in favor to liquid-liquid extraction technology tend to increase due to the lower energy and solvent consumption than extractive distillation. In any case, these results found cyclic carbonates as competitive mass separating agents, since recent advances in the literature using ionic liquids are less favorable [8].

Finally, liquid-liquid extraction is not feasible to separate cyclohexane and cyclohexene; however, the versatility of cyclic carbonates can overcome this limitation, changing the process to extractive distillation with Cyc-C, envisioning very competitive results concerning the ratio between purity standard and solvent consumption if one evaluates the literature [9].

4. Conclusions

This work exhaustively covers the use of CO₂-derived cyclic carbonates to separate hydrocarbon mixtures, namely {*n*-heptane + toluene}, {benzene + cyclohexane} and {cyclohexane + cyclohexene}. Firstly, properties of pure carbonates and an interaction analysis for {hydrocarbon + carbonate} binary mixtures have been studied by COSMO-RS method to envision the separations from a comparative point of view against conventional solvents as benchmark. Second step has been analyzed phase equilibria representative parameters regarding liquid-liquid extraction and extractive distillation processes, namely selectivity, distribution ratio and relative volatility by COSMO-based/Aspen computational approach. This has helped to conceptually open different application ways to test carbonates at process scale. Finally, carbonates have been screened at process scale to effectively narrow down CO₂-derived solvents to further study their suitability to meet commercial standards in a six-case approach structure, covering the three separations and the two processes.

Cyclic carbonates have shown a wide range of mixing behaviors with aromatics and aliphatics, covering from selective character to high capacity solvents; according with these interactions, there are some cyclic carbonates more appropriate to design liquid-liquid extraction processes and others to promote an extractive distillation approach. Extractive properties and relative volatilities of some cyclic carbonates are comparable or even superior to those for conventional solvents, namely sulfolane and NFM. At process scale and meeting commercial separations, energy and equipment demands have finally confirmed the suitability of these solvents as mass agents. Current results report cyclic carbonates as a wide family of competitive CO₂-derived designer solvents that contribute in the debate of new sustainable solvents to separate hydrocarbons. This new application can synergistically motivate the implementation of new and more sustainable processes to produce cyclic carbonates and envision a more favorable life cycle analysis.

Funding sources

The authors are grateful to Comunidad de Madrid (project P2018/EMT4348) and Ministerio de Economía y Competitividad of Spain (project CTQ2017-89441-R) for its financial support and Centro de Computación Científica de la Universidad Autónoma de Madrid (CCC) for its computational resources.

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.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.fuproc.2020.106639>.

References

- [1] R.I. Canales, J.F. Brennecke, Comparison of ionic liquids to conventional organic solvents for extraction of aromatics from aliphatics, *J. Chem. Eng. Data* 61 (5) (2016) 1685–1699.
- [2] C.J. Clarke, et al., Green and sustainable solvents in chemical processes, *Chem. Rev.* 118 (2) (2018) 747–800.
- [3] D.S. Sholl, R.P. Lively, Seven chemical separations to change the world, *Nature* 532 (2016) 435–437.
- [4] F. Chen, et al., High efficiency separation of olefin from FCC naphtha: influence of combined solvents and related extraction conditions, *Fuel Process. Technol.* 208 (2020).
- [5] P. Navarro, et al., Experimental screening towards developing ionic liquid-based extractive distillation in the dearomatization of refinery streams, *Sep. Purif. Technol.* 201 (2018) 268–275.
- [6] M. Larriba, et al., Choline chloride-based deep eutectic solvents in the dearomatization of gasolines, *ACS Sustain. Chem. Eng.* 6 (1) (2017) 1039–1047.
- [7] P. Navarro, et al., Dearomatization of pyrolysis gasoline by extractive distillation with 1-ethyl-3-methylimidazolium tricyanomethanide, *Fuel Process. Technol.* 195 (2019).
- [8] M. Ayuso, et al., Enhanced separation of benzene and cyclohexane by homogeneous extractive distillation using ionic liquids as entrainers, *Sep. Purif. Technol.* 240 (2020).
- [9] N. Delgado-Mellado, et al., Imidazolium and pyridinium-based ionic liquids for the cyclohexane/cyclohexene separation by liquid-liquid extraction, *J. Chem. Thermodyn.* 131 (2019) 340–346.
- [10] U. Domańska, et al., Separation of binary mixtures hexane/hex-1-ene, cyclohexane/cyclohexene and ethylbenzene/styrene based on limiting activity coefficients, *J. Chem. Thermodyn.* 110 (2017) 227–236.
- [11] H.G. Franck, J.W. Stadelhofer, *Industrial Organic Chemistry*, Springer-Verlag, 1988.
- [12] A. Vega, et al., Solvent selection for cyclohexane–cyclohexene–benzene separation by extractive distillation using non-steady-state gas chromatography, *Ind. Eng. Chem. Res.* 36 (3) (1997) 803–807.
- [13] Z. Salleh, et al., Efficient removal of benzene from cyclohexane-benzene mixtures using deep eutectic solvents – COSMO-RS screening and experimental validation, *J. Chem. Thermodyn.* 104 (2017) 33–44.
- [14] R.D. Rogers, K.R. Seddon, Ionic liquids—solvents of the future? *Science* 302 (5646) (2003) 792–793.
- [15] N.V. Plechkova, K.R. Seddon, Applications of ionic liquids in the chemical industry, *Chem. Soc. Rev.* 37 (1) (2008) 123–150.
- [16] M. Larriba, et al., Extraction of aromatic hydrocarbons from pyrolysis gasoline using tetrathiocyanatocobaltate-based ionic liquids: experimental study and simulation, *Fuel Process. Technol.* 159 (2017) 96–110.
- [17] M. Larriba, et al., Dearomatization of pyrolysis gasolines from mild and severe cracking by liquid-liquid extraction using a binary mixture of [4empy][Tf2N] and [emim][DCA] ionic liquids, *Fuel Process. Technol.* 137 (2015) 269–282.
- [18] I. Domínguez, E.J. González, Á. Domínguez, Liquid extraction of aromatic/cyclic aliphatic hydrocarbon mixtures using ionic liquids as solvent: literature review and new experimental LLE data, *Fuel Process. Technol.* 125 (2014) 207–216.
- [19] P.J. Scammells, J.L. Scott, R.D. Singer, Ionic liquids: the neglected issues, *Aust. J. Chem.* 58 (3) (2005) 155–169.
- [20] M.A.R. Martins, S.P. Pinho, J.A.P. Coutinho, Insights into the nature of eutectic and deep eutectic mixtures, *J. Solut. Chem.* 48 (7) (2018) 962–982.
- [21] Y. Hou, et al., Separation of toluene from toluene/alkane mixtures with phosphonium salt based deep eutectic solvents, *Fuel Process. Technol.* 135 (2015) 99–104.
- [22] W.-J. Jiang, et al., Manufacturing acidities of hydrogen-bond donors in deep eutectic solvents for effective and reversible NH₃ capture, *ACS Sustain. Chem. Eng.* 8 (35) (2020) 13408–13417.
- [23] N. Delgado-Mellado, et al., Thermal stability of choline chloride deep eutectic solvents by TGA/FTIR-ATR analysis, *J. Mol. Liq.* 260 (2018) 37–43.
- [24] B. Schäffner, et al., Organic carbonates as solvents in synthesis and catalysis, *Chem. Rev.* 110 (8) (2010) 4554–4581.
- [25] Q. Li, et al., Synthesis of propylene carbonate from urea and propylene glycol, *Stud. Surf. Sci. Catal.* (2004) 573–576.
- [26] Q. Li, et al., Synthesis of cyclic carbonates from urea and diols over metal oxides, *Catal. Today* 115 (1–4) (2006) 111–116.
- [27] T. Tabanelli, et al., Conversion of CO₂ to valuable chemicals: organic carbonate as green candidates for the replacement of noxious reactants, *Stud. Surf. Sci. Catal.* 178 (2019).
- [28] M. North, R. Pasquale, C. Young, Synthesis of cyclic carbonates from epoxides and

- CO₂, Green Chem. 12 (9) (2010) 1514–1539.
- [29] G. Fiorani, et al., Catalytic coupling of carbon dioxide with terpene scaffolds: access to challenging bio-based organic carbonates, ChemSusChem 9 (11) (2016) 1304–1311.
- [30] D. Bai, H. Jing, Aerobic oxidative carboxylation of olefins with metalloporphyrin catalysts, Green Chem. 12 (1) (2010) 39–41.
- [31] B. Schaffner, et al., Synthesis and application of carbonated fatty acid esters from carbon dioxide including a life cycle analysis, ChemSusChem 7 (4) (2014) 1133–1139.
- [32] J.-N. Xie, et al., One-pot stepwise synthesis of cyclic carbonates directly from olefins with CO₂ promoted by K₂S₂O₈/NaBr, J. CO₂ Util. 16 (2016) 313–317.
- [33] M.O. Sonnati, et al., Glycerol carbonate as a versatile building block for tomorrow: synthesis, reactivity, properties and applications, Green Chem. 15 (2) (2013) 283–306.
- [34] J.-Q. Wang, et al., Efficient fixation of CO₂ into organic carbonates catalyzed by 2-hydroxymethyl-functionalized ionic liquids, RSC Adv. 4 (5) (2014) 2360–2367.
- [35] Z. Zhang, et al., Glycerol carbonate as green solvent for pretreatment of sugarcane bagasse, Biotechnol. Biofuels 6 (2013) 153.
- [36] L. Moity, et al., Panorama of sustainable solvents using the COSMO-RS approach, Green Chem. (2012) 14(4).
- [37] M.C. Annesini, et al., Liquid-liquid equilibria for ternary systems containing hydrocarbons and propylene carbonate, J. Chem. Eng. Data 30 (2) (1985) 195–196.
- [38] S.H. Ali, et al., Extraction of aromatics from naphtha reformate using propylene carbonate, Fluid Phase Equilib. 214 (1) (2003) 25–38.
- [39] M.I. Zaretskii, V.V. Rusak, E.M. Chartov, Using propylene carbonate in extraction and absorption: a review, Coke Chem. 51 (3) (2008) 101–104.
- [40] R. Santiago, C. Moya, J. Palomar, Siloxanes capture by ionic liquids: solvent selection and process evaluation, Chem. Eng. J. 401 (2020).
- [41] R. Santiago, et al., Acetylene absorption by ionic liquids: a multiscale analysis based on molecular and process simulation, Sep. Purif. Technol. 204 (2018) 38–48.
- [42] J. Palomar, et al., Demonstrating the key role of kinetics over thermodynamics in the selection of ionic liquids for CO₂ physical absorption, Sep. Purif. Technol. 213 (2019) 578–586.
- [43] M. Larriba, et al., COSMO-based/Aspen Plus process simulation of the aromatic extraction from pyrolysis gasoline using the {[4empy][NTf₂] + [emim][DCA]} ionic liquid mixture, Sep. Purif. Technol. 190 (2018) 211–227.
- [44] V.R. Ferro, et al., Conceptual design of unit operations to separate aromatic hydrocarbons from naphtha using ionic liquids. COSMO-based process simulations with multi-component “real” mixture feed, Chem. Eng. Res. Des. 94 (2015) 632–647.
- [45] J. de Riva, et al., Aspen Plus supported conceptual design of the aromatic–aliphatic separation from low aromatic content naphtha using 4-methyl-N-butylpyridinium tetrafluoroborate ionic liquid, Fuel Process. Technol. 146 (2016) 29–38.
- [46] A.R. Ferreira, et al., Overview of the liquid–liquid equilibria of ternary systems composed of ionic liquid and aromatic and aliphatic hydrocarbons, and their modeling by COSMO-RS, Ind. Eng. Chem. Res. 51 (8) (2012) 3483–3507.
- [47] V.R. Ferro, et al., Enterprise ionic liquids database (ILUAM) for use in aspen ONE programs suite with COSMO-based property methods, Ind. Eng. Chem. Res. 57 (3) (2018) 980–989.
- [48] P. Navarro, et al., Stripping columns to regenerate ionic liquids and selectively recover hydrocarbons avoiding vacuum conditions, Ind. Eng. Chem. Res. 58 (44) (2019) 20370–20380.
- [49] A.I. Papadopoulos, et al., Computer-Aided Molecular Design: Fundamentals, Methods, and Applications, in Reference Module in Chemistry, Molecular Sciences and Chemical Engineering, Elsevier, 2018.
- [50] C. Gertig, K. Leonhard, A. Bardow, Computer-aided molecular and processes design based on quantum chemistry: current status and future prospects, Curr. Opin. Chem. Eng. 27 (2020) 89–97.
- [51] G.W. Meindersma, A.J.G. Port, A.B. de Haan, Ternary liquid–liquid equilibria for mixtures of toluene + n-heptane + an ionic liquid, Fluid Phase Equilib. 247 (1–2) (2006) 158–168.
- [52] J. Andzelm, C. Kölmel, A. Klamt, Incorporation of solvent effects into density functional calculations of molecular energies and geometries, J. Chem. Phys. 103 (21) (1995) 9312–9320.
- [53] A. Klamt, Conductor-like screening model for real solvents: a new approach to the quantitative calculation of solvation phenomena, J. Phys. Chem. 99 (7) (1995) 2224–2235.
- [54] TURBOMOLE 4.4.1, A Development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989–2007, TURBOMOLE GmbH, since 2007, available from, 2019. <http://www.turbomole.com>.
- [55] C.B. Castells, D.I. Eikens, P.W. Carr, Headspace gas chromatographic measurements of limiting activity coefficients of eleven alkanes in organic solvents at 25 °C. 1, J. Chem. Eng. Data 45 (2) (2000) 369–375.
- [56] M. Toppf, D. Gruber, J. Gmehling, Measurement of activity coefficients at infinite dilution using gas–liquid chromatography. 10. Results for various solutes with the stationary phases dimethyl sulfoxide, propylene carbonate, and N-ethylformamide, J. Chem. Eng. Data 44 (6) (1999) 1355–1359.
- [57] S. Zhang, et al., Infinite dilution activity coefficients in ethylene glycol and ethylene carbonate, J. Chem. Eng. Data 48 (1) (2003) 167–170.
- [58] I. Garcia, et al., Thermodynamics of binary mixtures containing organic carbonates. 1. Excess enthalpies of dimethyl carbonate + hydrocarbons or + tetra-chloromethane, J. Chem. Eng. Data 33 (4) (1988) 423–426.
- [59] J. Lohmann, R. Böltz, J. Gmehling, Excess enthalpy data for seven binary systems at temperatures between 50 and 140 °C, J. Chem. Eng. Data 46 (2) (2001) 208–211.
- [60] M.C. Annesini, et al., Excess enthalpy and T-x data of aromatic-propylene carbonate mixtures, J. Chem. Eng. Data 29 (1) (1984) 39–41.
- [61] S.-T. Lin, S.I. Sandler, A priori phase equilibrium prediction from a segment contribution solvation model, Ind. Eng. Chem. Res. 43 (5) (2002) 899–913.
- [62] A.B.S.H. Salem, Liquid-liquid equilibria for the systems triethylene glycol - toluene - heptane, propylene carbonate - toluene - heptane and propylene carbonate - o-xylene - heptane, Fluid Phase Equilib. 86 (1993) 351–361.
- [63] J.-J. Li, et al., Liquid–Liquid equilibria for the systems: heptane + benzene + solvent (propylene carbonate, N,N-dimethylformamide, or mixtures) at temperatures from (303.2 to 323.2) K, J. Chem. Eng. Data 59 (11) (2014) 3307–3313.
- [64] Y. Wang, et al., Design optimization and operating pressure effects in the separation of acetonitrile/methanol/water mixture by ternary extractive distillation, J. Clean. Prod. 218 (2019) 212–224.
- [65] K. Kulajapeng, U. Suriyapraphadilok, R. Gani, Systematic screening methodology and energy efficient design of ionic liquid-based separation processes, J. Clean. Prod. 111 (2016) 93–107.
- [66] Huntsman, JEFFSOL Alkylene Carbonates, Huntsman Corporation, 2001, <http://www.huntsman.com>.
- [67] UBE, Informe de Seguridad de Producto de Carbonato de glicerina, UBE Corporation Europe, S.A.U, 2017 <https://www.ube.es/ES/sostenibilidad/pdfs/PSS-for-Glycerine-carbonate.pdf>.
- [68] M.A. Rasool, P.P. Pescarmona, I.F.J. Vankelecom, Applicability of organic carbonates as green solvents for membrane preparation, ACS Sustain. Chem. Eng. 7 (16) (2019) 13774–13785.
- [69] T. Yang, et al., Densities and viscosities of N-formylmorpholine (NFM) + p-xylene, + o-xylene, + m-xylene at different temperatures and atmospheric pressure, J. Chem. Eng. Data 52 (5) (2007) 2062–2066.
- [70] U. Tilstam, Sulfolane: a versatile dipolar aprotic solvent, Org. Process Res. Dev. 16 (7) (2012) 1273–1278.
- [71] P. Navarro, et al., Selective recovery of aliphatics from aromatics in the presence of the {[4empy][Tf₂N] + [emim][DCA]} ionic liquid mixture, J. Chem. Thermodyn. 96 (2016) 134–142.
- [72] Environmental Protection Agency (US EPA), Chemical Data Reporting (CDR), (2016).