



Full Length Article

Fine-tune simultaneous dearomatization, desulfurization and denitrogenation of liquid fuels with CO₂-derived cyclic carbonates

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ABSTRACT

In this work, eight CO₂-derived cyclic carbonates, namely ethylene carbonate (Eth-C), propylene carbonate (Pro-C), butylene carbonate (But-C), hexylene carbonate (Hex-C), cyclohexene carbonate (Cyc-C), styrene carbonate (Sty-C), glycerol carbonate (Gly-C) and (Chloromethyl)ethylene carbonate (Chl-C) were evaluated as solvents to mitigate residual aromatic content in liquid fuels by envisioning an efficient liquid-liquid extraction process, using benzene, thiophene and pyrrole as benchmark compounds for dearomatization, desulfurization and denitrogenation processes. After evaluating at molecular scale by COSMO-RS method (activity coefficients and excess enthalpies of aromatic-cyclic carbonate mixtures), predictions of phase equilibria of ternary systems involving *n*-heptane are carried out by COSMO-based/Aspen methodology for evaluating the extractive properties of studied cyclic carbonates. Then, computational findings are experimentally validated for the representative Pro-C case through multicomponent liquid-liquid equilibria. Finally, the complete separation process was simulated by COSMO-based/Aspen methodology to evaluate solvent losses in extraction and distillation units, energy consumption, and aromatic purity for process specifications aimed at enhancing gasoline purity and recovery. Main results suggest that Pro-C provides promising process performance at a very competitive solvent to feed (S/F) ratio and specific energy consumption, positioning cyclic carbonates for studied separation.

1. Introduction

The development of new generation solvents is of utmost interest to purify liquid fuels [1]. Current technology is unable to clean exhaustively treated refinery streams, imposing the requirement of further purification before its use. The research community is presenting ionic liquids (ILs) and eutectic solvents (ESs) as more compatible solvents, drawing a sustainable picture to improve the specifications of these industrial streams [2].

ILs impose the well-known advantages of negligible vapor pressure and designer solvents capacity with tunable extractive and physical properties [3]. In the separation of remained aromatics, namely benzene, thiophene and pyrrole, ILs have been tested exhaustively, showing improved extractive properties than benchmark organic solvents, such as sulfolane, and stating that benzene is the key component in the search of new solvents [4–10]. It is relevant to highlight that there were few but different strategies at process scale to extract aromatics from low

aromatic streams. Since benzene is the key component in the operation, the next strategies are exemplified to the extraction of this compound: i) using selective ILs, namely those composed by [SCN][−] and [DCA][−] anions [11]; ii) selecting ILs with remarkable capacity of extraction, in mass basis, such as [4bmpy][TCM] [12]. Results indicated that high capacity ILs impose a more feasible strategy due to the large recycling streams of aromatics associated with a selective IL. Therefore, the use of a high capacity IL, such as [4bmpy][TCM], stands out as the best alternative to purify not only the liquid fuel but also the extracted aromatics to prevent non-aromatic losses. Even with these possibilities, the IL price clearly determine the use of these solvents as a scalable option for the industry in the near future and solvent losses in the liquid fuel, although low, could be relevant in terms of fuel specification, as can be noticed in the literature [13].

ESs introduce a concept that enables the use of room temperature solids at liquid state by the formation of a eutectic mixture with a tunable depression of the melting point as function of the ES constituents

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or its composition. At least two compounds are required, a hydrogen bond donor (HBD) and a hydrogen bond acceptor (HBA). When the depression of the melting point is much higher than that predicted by ideal solid–liquid equilibrium, the concept of deep eutectic solvents stands out [14]. In both cases, this class of solvents allows a tunable and cost-effective approach when selecting platform constituents or conventional compatible organic compounds, such as choline chloride, levulinic acid, ethylene glycol or glycerol, among an uncountable number of species [15]. Recently, Kroon and coworkers [16,17,18] have extensively tested ES in eliminating aromatics from diesel models and gasolines, covering a wide collection of HBD and HBA through massive parametric studies and, thus, an interesting range of extractive and physical properties to develop ES-based technologies. The irruption of ES has motivated a recent review on this topic, conducted by Tahir and coworkers [19]. Although ESs stand as a helpful concept in the search for new solvents in this field, the mature of this approach is far from process scale and even further from industrial application. The liquid range of the vast majority of ES is narrow, limiting regeneration steps by distillation and making complex to develop conceptual designs that support reusability [20,21]. In addition, sometimes ESs are optimized forgetting the compatible and low-cost target criteria of the constituents, which mitigates the interest of using ES instead of ILs, failing in the same drawbacks as ionic species [22].

Recently, cyclic carbonates stood as a more compatible organic solvents formulated by CO₂ [23]. The advance in the CO₂-based cyclic carbonates development has three main open research challenges. First, the conceptual process designs are continuously being improved, using sustainable homogeneous or heterogeneous catalysts, dealing with competitive energy consumptions and related emissions [24]. Second, epoxides are improving their synthesis routes simultaneously with the emergence of the bioepoxide concept, which imposes that the near future can provide biocarbonates from natural resources and CO₂ [25]. Third, cyclic carbonates are versatile compounds for the industry, ranging from monomers in the plastic industry to final products with solvent potential [23]. Cyclic carbonates present good extractive properties for hydrocarbon processing [26] and designer solvent character [27], together with good transport properties and low volatility, whereas they are CO₂ neat consumers. This context draws an ideal and compensates picture for a world demanding routes to use CO₂ as building block.

In this work, a systematic study was proposed to evaluate cyclic carbonates as extracting solvents to fine-tune residual aromatics in liquid fuels. In order to describe a wide range of fuels, *n*-heptane was selected as the matrix, since its solubility in any solvent is greater than heavier alkanes, i.e. isooctane or *n*-decane, [28] imposing transferability of the conclusions from gasolines to heavier fuels when the findings would be feasible for *n*-heptane. Regarding aromatics, benzene, thiophene and pyrrole are selected as the most studied benchmark compounds in the literature in the dearomatization, desulfurization and denitrogenation separation modelling, trying to provide a benchmark scenario to ease the comparison of neoteric and conventional solvents. However, other S-containing compounds are also studied to properly show how cyclic carbonates can work with a broad scope of persistent non-desirable hydrocarbons. The work is structured following a multi-scale approach which integrates next steps: i) molecular level exploration by COSMO-RS method, which has been widely validated in the selection of ILs and ES for these separations; ii) *ad hoc* experimental validation for selected representative solvent (Pro-C); and iii) process modelling and simulation using COSMO/Aspen methodology, successfully applied previously for the conceptual design and techno-economical evaluation of dearomatization, desulfurization and denitrogenation of fuels by liquid–liquid extraction using ILs and other solvents. This structure allows to quickly moving from molecular level to process scale, optimizing the functionalization of the solvent at process scale. Discussing the pros and cons of distribution ratios or selectivities without a process specification set does not allow to properly selecting a

solvent, whereas COSMO/Aspen methodology helps to evaluate directly solvents at process scale. Following this approach, firstly, COSMO-based analysis is applied to evaluate the thermodynamics of involved cyclic carbonate-aromatic mixtures, by means of calculations of activity coefficient, excess enthalpy and liquid–liquid equilibrium data. Then, computational findings are validated by experimental determination of extractive properties for the benchmark solvent Pro-C. Finally, process modelling using COSMO/Aspen methodology allows evaluating the process performance of studied cyclic carbonates to simultaneously separate benzene, thiophene and pyrrole from *n*-heptane by liquid–liquid extraction, in terms of solvent and specific energy consumptions. Finally, once selected the most promising cyclic carbonate, it is used in the fine design of the separation process attending to its specific features.

2. Computational and experimental details

2.1. Molecular geometry optimization

The eight cyclic carbonates, presented in Table 1, were optimized using Turbomole 7.4 software until their minimum energy with BP86/TZVP computational level, using the COSMO continuum solvation method. After that, a single point calculation avoids negative vibrational frequencies for non-optimized cases, providing *.cosmo file required as input in COSMOtherm software.

2.2. Extractive properties predictions using COSMO-based models

The interaction of cyclic carbonates and selected aromatics was evaluated through the activity coefficients at infinite dilution calculated at 25 °C by COSMO-RS method using COSMOtherm v.19 software with its implicit parametrization BP_TZVP_19. COSMO-RS stands as one of the preferred options to screen solvents together with other tools as QSPR [29], with the major advantage of the transferability from molecular level to process simulation only using an optimized molecule together with sigma profile and COSMO volume, all estimated properties. In addition to this, excess enthalpies of equimolar cyclic carbonate-aromatic systems were calculated at 25 °C in order to obtain a deeper insight of the intermolecular interactions determining the mixture behavior; previous works on cyclic carbonates-aromatic mixtures

Table 1

Cyclic carbonates names, abbreviations, chemical structures and boiling temperatures.

Compound	Alias	Structure	Boiling temperature*/K
(Chloromethyl)ethylene carbonate	Chl-C		647
Styrene carbonate	Sty-C		675
Butylene carbonate	But-C		570
Cyclohexene carbonate	Cyc-C		627
Glycerol carbonate	Gly-C		588
Hexylene carbonate	Hex-C		595
Propylene carbonate	Pro-C		571
Ethylene carbonate	Eth-C		517

*Predicted by COSMO-RS.

suggest that entropic contribution can be simplified in the analysis [26].

Finally, the activity coefficients of cyclic carbonates in *n*-heptane were evaluated to draft the solvent losses in the liquid–liquid extractor as function of the solvent structure.

2.3. Experimental validation

Multicomponent liquid–liquid extraction experiments were done to validate the results obtained using COSMO/Aspen methodology at process scale. S/F ratios of 1, 2 and 3 were fixed for feeds composed of *n*-heptane and 1000 ppms of each aromatic, namely benzene, thiophene and pyrrole. The specification of chemicals is included in Table 2.

The raffinate and extract phases were analyzed by GC using an Agilent 6890 N GC System with a GC column Agilent HP-50 (30 m × 0.320 mm). The analysis of both phases employed a He flow of 1.0 mL/min and oven temperature of 40 °C for 9 min followed by a temperature ramp of 20 °C/min to 200 °C for a total of 15 min.

2.4. Process modelling and simulation

Case 1. Extractive properties calculation and validation

Aspen Plus (V11) was used to evaluate aromatic distribution ratio (K ; eq.1) and aromatic/*n*-heptane selectivity (S ; eq. (2)) through ternary diagram building for all {*n*-heptane + aromatic + cyclic carbonate} cases. The cyclic carbonates were introduced as pseudocomponents following the COSMO/Aspen methodology reported elsewhere [27]. The cyclic carbonates are implemented in Aspen Plus as pseudo-components by defining their sigma-profiles, as well as their molecular weight, density, boiling point and COSMO volume, previously calculated using COSMOtherm software. COSMO-SAC property method as implicit in Aspen Plus was selected for all the calculations.

$$K = \frac{x_2^E}{x_2^R} \quad (1)$$






$$S = \frac{x_2^E \cdot x_1^R}{x_2^R \cdot x_1^E} \quad (2)$$

In order to validate the predictions of the COSMO-SAC property method, aromatics recovery employing Pro-C as extracting solvent was calculated. For this purpose, a decanter unit was used at different S/F ratios.

Case 2. Solvent screening

Scheme 1 shows the proposed flowsheet deployed in Aspen Plus process simulator. The process consists of a countercurrent multi-stage liquid–liquid extraction column to extract benzene, thiophene and pyrrole from *n*-heptane, a stripping column to eliminate the *n*-heptane

Table 2
Specification of Chemicals.

Chemical	Structure	Supplier	Purity/ %	CAS	MW	MP /°C
Benzene		MERCK	>99.7 GC	71- 43-2	78.11	80
Thiophene		Sigma- Aldrich	>99 GC	110- 02-1	84.14	84
Pyrrole		Sigma- Aldrich	>98	109- 97-7	67.09	129
<i>n</i> -Heptane		Sigma- Aldrich	>99 GC	142- 82-5	100.21	98
Propylene carbonate		Sigma- Aldrich	>99.7 GC	108- 32-7	102.09	242

dragged with the solvent as the superior configuration found in the literature [26] and a final distillation column to regenerate the solvent and to obtain the aromatic stream. The process operates at atmospheric pressure to avoid vacuum costs.

The extractor (Extract model in Aspen Plus) is fed with untreated gasoline (UG) with a mass flow of 100 kg/h of mainly *n*-heptane -impurified with 1000 ppms of each aromatic (benzene, thiophene and pyrrole)- and a cyclic carbonate stream (S). The aromatic content is expressed as mass-based ppms. The solvent flow varies to satisfy the benzene specifications in the clean gasoline (CG), which is directly obtained from the top of the column without further processing. The solvent consumption is adjusted to meet 99% of benzene recovery in the column as benzene is the key component in the extraction, allowing to reduce the three aromatics content below 100 ppms. On the other hand, the aromatics and the solvent are fed to a stripping column, recycling the non-aromatics stream obtained on the top of the extraction column. The recovery of 99% of dragged *n*-heptane is imposed, varying the distillation flow. The solvent and the aromatics are separated in a distillation column, specifying a 95% recovery of pyrrole since it is the heaviest aromatic to be removed from the cyclic carbonate. Boiling temperatures of all cyclic carbonates are high enough to perform the pyrrole/solvent separation. Stripping and distillation columns are described with Rad-Frac model in Aspen Plus. All the specifications fixed in each operation stages are shown in Table 3. These initial specifications are related to previous works on the use of cyclic carbonates as extracting agents [26,27].

Case 3. Improved process against benchmark process

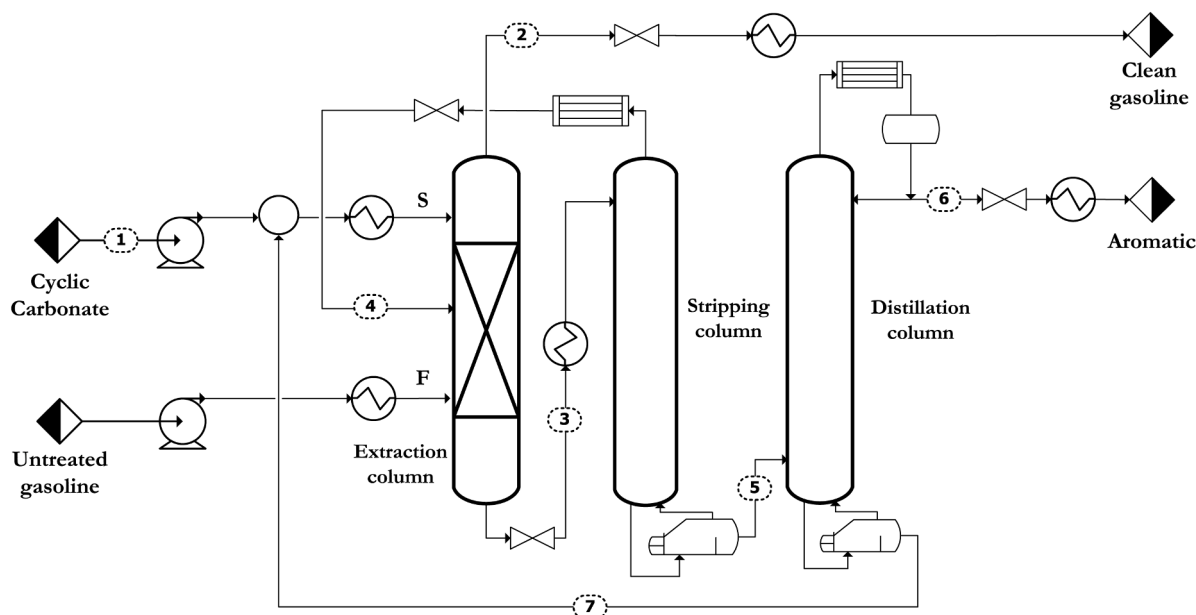
Following the above scheme, pyrrole recovery is modified to reduce solvent losses during the final distillation devoted to separate aromatics and regenerate the solvent. In addition, a further simulation is carried out with sulfolane as reference solvent for comparison purposes. Finally, a sensitivity analysis was deployed to draft a configuration that minimizes specific energy consumption using Pro-C.

3. Results

3.1. Activity coefficients and excess enthalpies of cyclic carbonate + hydrocarbon mixtures

In order to understand the interaction between the solutes, namely benzene, thiophene and pyrrole, and cyclic carbonates, Fig. 1 displays the activity coefficient of these aromatics at infinite dilution in the studied cyclic carbonate solvents together with these data related to the matrix model, *n*-heptane. As can be seen, pyrrole shows a more favorable interaction with the solvents (lower activity coefficient value), followed by benzene and thiophene with similar behaviors. This fact is in agreement with literature [12] but here demonstrated with a new solvent collection. Exploring other S-containing compounds (see Figure S1 in the Supplementary Material), it is found that thiophene is a representative S-containing hydrocarbon to be removed from liquid fuels. In fact, the cyclic carbonate nature has a higher impact on the activity coefficient of the S-containing hydrocarbon than its nature, since $\ln \gamma$ of thiophene range from 4 to 0.1, whereas the S-containing structure imposes a lower variation between 0 and 1.6.

Regarding the matrix, even a short alkyl chain length linear alkane as *n*-heptane suggests that the extraction is quite favorable in terms of selectivity. Moving from activity coefficients to interaction energy analysis, the excess enthalpies are shown in Fig. 2. Observing the similar trends with activity coefficient values of Fig. 1, it is concluded that the mixture behavior is governed by enthalpy, in good agreement with previously achieved conclusion for cyclic carbonate-aromatic systems [26]. The mixture with all cyclic carbonates shows decreasing endothermic behavior in the order *n*-heptane > benzene > thiophene, whereas the mixtures with pyrrole are exothermic. In addition, the molecular structure of cyclic carbonate plays a main role in the mixture behavior with aromatics, COSMO-RS calculations revealing more



Scheme 1. Flowsheet of the proposed process to clean gasolines using cyclic carbonates.

Table 3
Equipment specifications of the proposed process.

Equipment	Spec	Value
Extraction column	Temperature (°C)	25
	Stages	5
	Solvent feed stage	1
	Naphtha feed stage	5
	Recycle feed stage	3
	Benzene recovery	99%
Stripping column	Stages	5
	Feed stage	1
	Aliphatic recovery on top	99%
Distillation column	Stages number	10
	Feed stage	5
	Reflux ratio	5
	Pyrrole recovery on top	95%

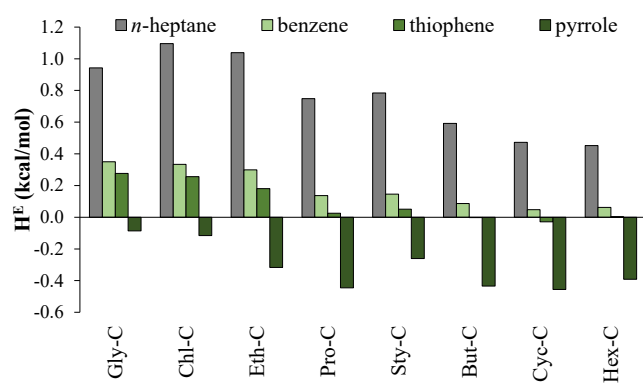


Fig. 2. Excess enthalpies of equimolar hydrocarbon + cyclic carbonate binary systems at equimolar proportions.

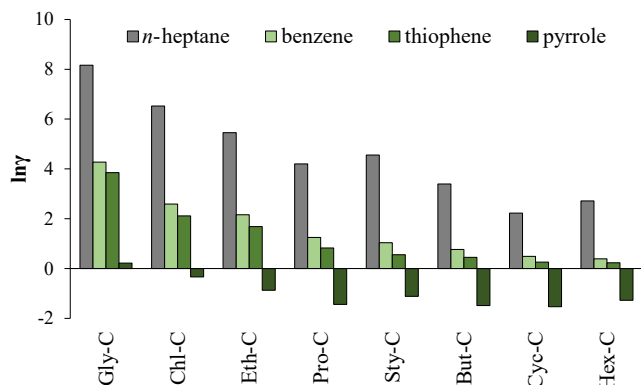


Fig. 1. Activity coefficients of hydrocarbons at infinite dilution in hydrocarbon + cyclic carbonate binary systems.

thermodynamically favored mixing in the order Hex-C > Cyc-C > But-C > Sty-C > Pro-C > Eth-C > Chl-C > Gly-C. The use of cyclic carbonates has been successfully tested for BTEX extraction from low aromatic content naphtha and toluene or benzene extraction from *n*-heptane or cyclohexane, respectively, with less selective interactions [27,26].

Considering that the fuel model is very diluted of aromatics, the closer and more selective interactions between benzene, thiophene and pyrrole with the solvents described by COSMO-RS method supports the evaluation of the ternary phase equilibria comprising aromatic + *n*-heptane + cyclic carbonate, and thus, the extractive properties.

Finally, the cyclic carbonate activity coefficients in *n*-heptane are shown in Fig. 3 to corroborate that the solvents with a more specific interaction with the aromatics and more repulsive with the alkane will be the more desirable to meet low solvent losses in the extractor.

3.2. Extractive properties of cyclic carbonate + hydrocarbon mixtures

COSMO-based/Aspen approach provides phase equilibria predictions at 40 °C, shown in Fig. 4 for three representative solvent cases (Gly-C, polar; Pro-C, intermediate; Hex-C, non-polar) and two solutes (benzene and pyrrole), being collected in Figure S2 of Supplementary Material the remaining systems from all aromatic-solvent combinations. As inferred from Fig. 4, the functionalization of the cyclic carbonate can strongly modulate the solubility of the aromatic and the alkane matrix, therefore extractive properties are fine-tuned by changing the solvent. In addition, benzene and thiophene display equivalent behaviors, being the key components in the extraction, whereas pyrrole can be easily

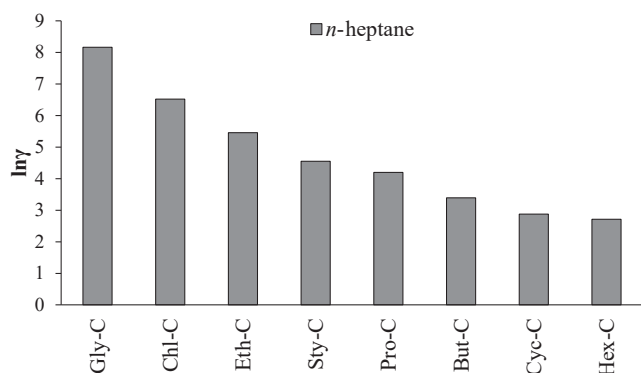


Fig. 3. Representation of the cyclic carbonate activity coefficients in *n*-heptane at infinite dilution, calculated at 25 °C.

separated from the non-aromatic independently of the solvent nature. On the other hand, the alkane solubility is entirely dependent in the solvent polarity for all solute cases, increasing in the order Cyc-C > Hex-C > But-C > Sty-C > Eth-C > Pro-C > Chl-C > Gly-C.

Moving from phase diagrams to extractive properties (see Fig. 5 for

benzene/pyrrole/thiophene + *n*-heptane + cyclic carbonate systems), the key component, benzene, shows at very low concentration favorable distribution ratios and selectivities ranging from 0.15 to 1.1 and 150 to 10, respectively, close to the extractive properties predicted for thiophene, whereas pyrrole solute will be much easily extracted using cyclic carbonates, attending to the high *K* and *S* values calculated by COSMO-based/Aspen methodology.

A wide range of extractive property values is obtained depending on cyclic carbonate structure, generally found opposite trends in *K* and *S* values, in good agreement with previous results for IL and ES solvents [1,2]. Therefore, the selection of the best extractive properties for a solvent is a task devoted to process scale, aiming at reducing energy and chemical consumption.

After showing that cyclic carbonates may be suitable solvents to adjust the remaining aromatics in liquid fuels, an *ad hoc* experimental validation using the representative case of Pro-C is carried out for the oil model considered in this work. Table 4 compares experimental and calculated distribution coefficients of benzene -as key component of separation- in Pro-C as function of mass-based S/F ratio considering a model oil composed by *n*-heptane and by 1000 ppm of each aromatic at 298 K. As can be seen, computational approach predicts reasonably *K* values of the key compound of the extraction, in good agreement with

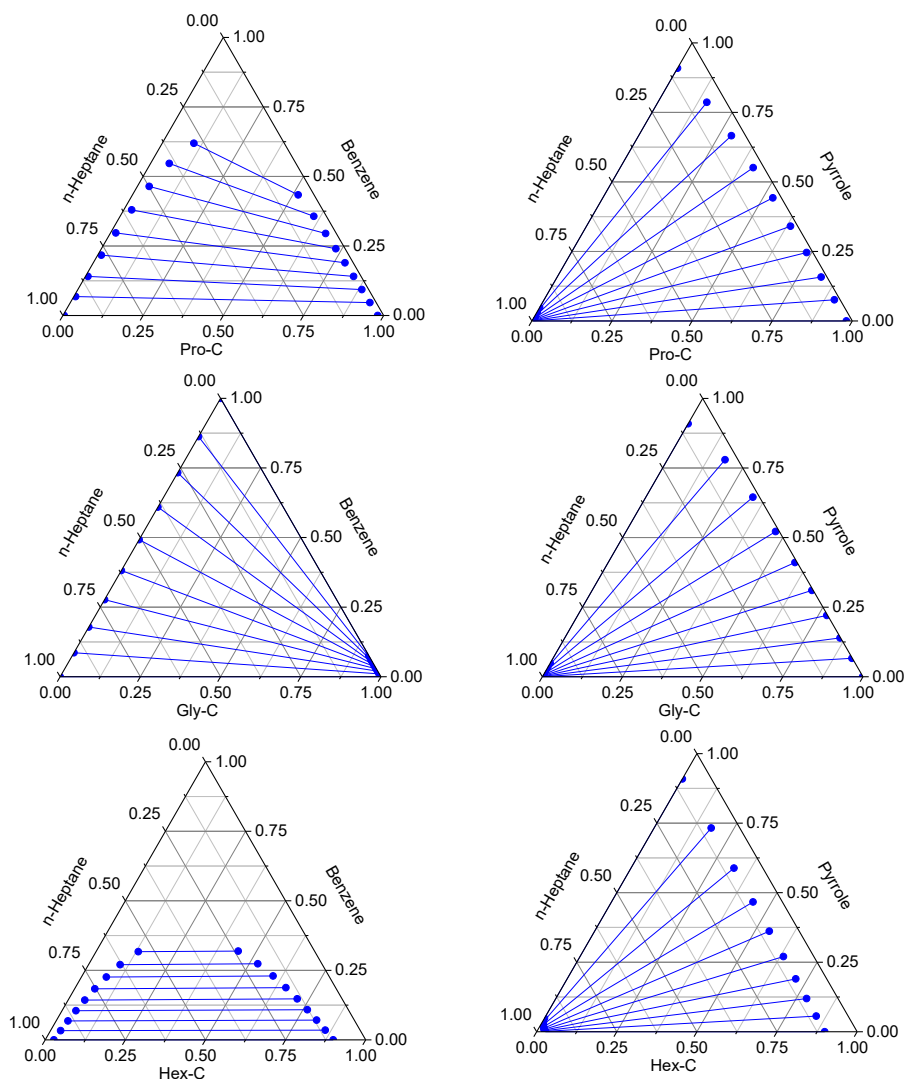


Fig. 4. Phase diagram of representative aromatic + *n*-heptane + cyclic carbonate cases.

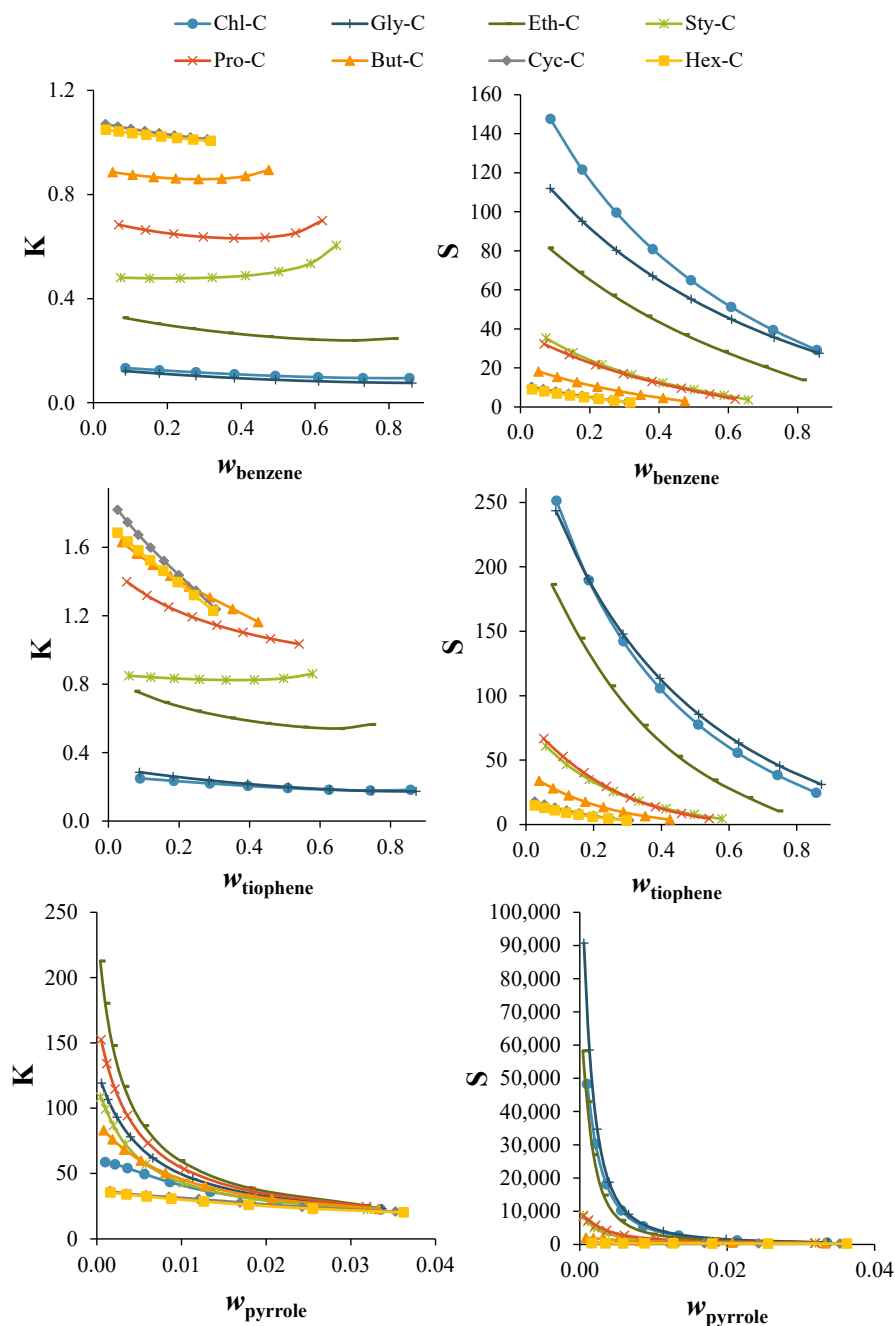


Fig. 5. Extractive properties of aromatics + n-heptane + cyclic carbonate cases predicted by COSMO-SAC: aromatic distribution ratios (K) and aromatic/n-heptane selectivities (S).

Table 4

Experimental/calculated distribution ratios of benzene in Pro-C as function of S/F ratio within a model oil formed by n-heptane and 1000 ppms of each aromatic and at 298 K.

S/F	Experimental K_{benzene}	COSMO-SAC K_{benzene}
1	0.65	0.703
2	0.67	0.705
3	0.68	0.706

the reported predictability of COSMO-based/Aspen approach for similar ternary systems using other solvents [26]. To complete experimental validation, Table 5 collects a comparison of aromatic recovery by

liquid–liquid extraction using Pro-C solvent as function of S/F ratio from experimental and COSMO/Aspen methodology (Simulation Case I in Computational and Experimental Details section). As a key component, benzene is appropriately modelled by COSMO-based/Aspen approach as well as this model properly captures the behavior of the other two aromatics. Therefore, the experimental results corroborate the findings obtained from COSMO/Aspen methodology, and Pro-C –as benchmark cyclic carbonate– is experimentally validated as a potential solvent to purify liquid fuels.

3.3. Process scale evaluation of cyclic carbonates in the simultaneous extraction of benzene, thiophene and pyrrole from a gasoline model

The simultaneous separation of the three aromatics from n-heptane

Table 5

Experimental/calculated benzene, thiophene and pyrrole recovery in Pro-C as function of S/F ratio considering a model oil composed by *n*-heptane and by 1000 ppm of each aromatic and at 298 K.

Recovery (%)	Source	S/F		
		1	2	3
Benzene	COSMO-SAC	43.2	60.7	70.3
	Experimental	33.9	50.0	61.9
Thiophene	COSMO-SAC	61.5	76.5	83.3
	Experimental	51.9	66.3	72.2
Pyrrole	COSMO-SAC	99.8	99.9	99.9
	Experimental	95.2	97.3	98.3

in the typical concentration of the industrial problem is modelled using COSMO/Aspen methodology following the specifications claimed in Section 2.5 (Simulation Case II), using the 8 cyclic carbonates included in this work. The four parameters evaluated at process scale (Figs. 6 and 7) are i) solvent and energy consumption (Fig. 6); and ii) solvent losses in raffinate (2 in Scheme 1) and in aromatic stream (6 in Scheme 1) plotted in Fig. 7. As can be seen in Fig. 6A, several cyclic carbonates show competitive S/F ratios to adjust aromatic content in the model oil to negligible values, related to their high distribution coefficients of solute between aliphatic-rich raffinate and solvent-rich extract phases. Separation process using these cyclic carbonates (namely Pro-C, Eth-C, But-C and Sty-C) with lower solvent requirement also needs lower specific energy consumption (Fig. 6B).

Moving to Fig. 7, selectivity presents a dominant role when inspecting the solvent losses in *n*-heptane-rich raffinate phase, since the more repulsive interaction of *n*-heptane and the solvent provides negligible losses. From the list of four candidates with favorable energy consumption, Eth-C followed by Sty-C and Pro-C are the three solvents with reasonable losses in the raffinate. Moving to the solvent losses in aromatic stream (6 in Scheme 1) -which are related to the vapor pressures of the cyclic carbonates-, it is highlighted that Pro-C followed by But-C and Eth-C are the worst cases. However, final distillation to separate the aromatics from the solvent can be tuned independently for each cyclic carbonate, avoiding these solvent losses. The heavier aromatic is pyrrole, which is completely soluble in all cyclic carbonates; relaxing the pyrrole recovery in the distillate, the solvent consumption of the process is not changing at all.

The results pointed out that Pro-C and Eth-C are the most promising solvents; the former presents lower energy consumption, whereas the latter can develop a cleaner technology since their losses in the raffinate stream are lower. Since organic carbonates are well-known additives to fuels to increase their quality through the octane number [30], the energy criterion stands out as the more adequate, narrowing to Pro-C the screening of cyclic carbonates. In comparison with other compounds

such as ILs or ES, this point reveals an additional advantage for cyclic carbonates when designing extraction processes.

From a process design point of view, we can discuss three different behaviors. Selective cyclic carbonates, which are those with polar groups (Chl-C and Gly-C), allow reducing solvent losses in the raffinate but demand high S/F ratios due to the low distribution ratios, thus imposing high-energy requirements. High capacity cyclic carbonates, those with non-polar substituents (Hex-C and Cyc-C), reduce S/F ratios but energy consumption is not competitive since recycling streams related to the dragged aliphatic are larger than the other kind of cyclic carbonates; this last fact, together with the higher losses in the raffinate, imposes low competitiveness. Finally, cyclic carbonates with an intermediate behavior due to short alkyl chain length substituents, represented by selected Pro-C), allow optimizing energy consumption with reasonable S/F ratios and solvent losses, respectively.

3.4. Further development of propylene carbonate process and evaluation against sulfolane benchmark solvent

Further calculations were carried out (Simulation Case III) to adjust the final distillation to regenerate Pro-C, with the aim of reach negligible solvent losses, being the proposal design of interest for cleaning liquid fuels. In order to tune the Pro-C losses, the aromatic separation from the solvent in the regeneration step is achieved by changing the pyrrole recovery from 95 % to 10 %, with a full recovery of benzene and thiophene. Pyrrole is completely soluble in the solvent, and it does not affect the fresh solvent consumption of the process when a slight accumulation is done to reduce solvent losses in the regeneration step. Summarizing, the final process for Pro-C, the extraction permits to adjust benzene content from 1000 to 100 ppm in the case of benzene, whereas thiophene concentrations locates below 10 ppm and the remained content of pyrrole is negligible (below 1 ppb). The extract stream dragged 23.8 kg/h of *n*-heptane, recovering almost all in the stripping column to minimize the *n*-heptane losses below 0.6 % (calculated as the difference between the raffinate –stream 2- and the feed stream).

In order to demonstrate the role of cyclic carbonates in comparison with traditional organic solvents, a comparison of Pro-C and sulfolane is accomplished. Table 6 reports the two characteristic process performance parameters for both solvents, leaving aside the losses by distillation since they are negligible in both cases and the solvent consumption imposed in both simulations (2.3). As seen, the use of Pro-C enhances energy efficiency and avoids massive solvent losses. Solvent losses are essential from a solvent cost point of view as recently discussed [31]. Pro-C losses are lower than those of sulfolane, clearly pointing that OPEX related to Pro-C make up will be lower since solvent price is lower than that of sulfolane. Pro-C price is round 1–3 \$/kg [32], whereas sulfolane price is over 30 \$/kg [31]. In addition, since S/F ratio

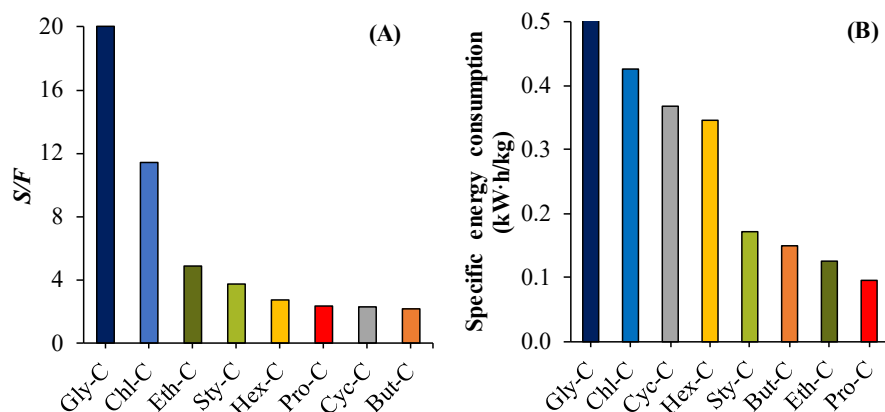


Fig. 6. Solvent to feed ratios, S/F, and specific energy consumption of the process for each cyclic carbonate process.

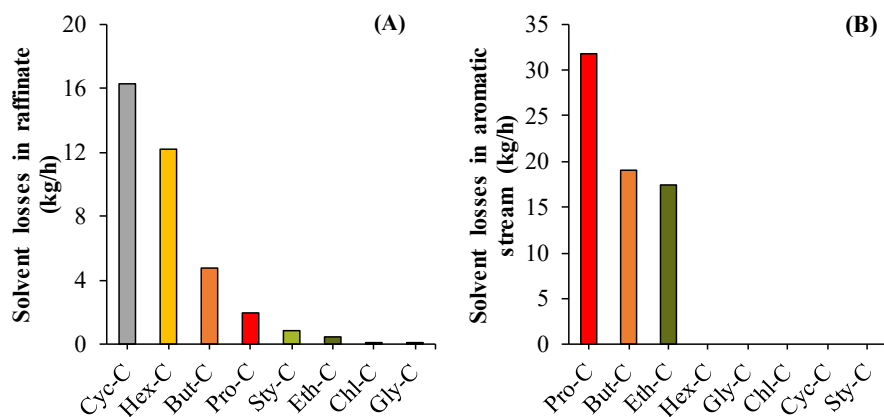


Fig. 7. Solvent losses in raffinate and in aromatic stream for each cyclic carbonate.

Table 6

Comparison of process insights for propylene carbonate and sulfolane.

Solvent	Losses in raffinate (kg/h)	Specific energy consumption (kWh/kg)
Pro-C	1.956	0.206
Sulfolane	34.812	0.560

is lower using Pro-C than sulfolane to meet the separation criteria, CAPEX are again better for Pro-C. Finally, the solvent change in favor to Pro-C clearly reduces energy consumption, which is larger in terms of economic impact. CO₂-derived cyclic carbonates use CO₂ within a low energy demanding process, even expecting a more competitive price in the near future. Extending the comparison to other neoteric solvents, ILs and ESs are expected to increase CAPEX due to the higher S/F ratios found in the literature and/or higher prices [1,2,31], whereas lower solvent losses would be a positive point for ILs and ESs as part of the OPEX. However, the compatibility of cyclic carbonates and treated fuel is a key advantage to support this proposal.

A final sensitivity analysis was done to improve process configuration and, thus, minimize specific energy consumption. The evolution of this objective function with *n*-heptane recovery in the top of the stripping column and the reflux ratio and pyrrole recovery in the distillate stream is collected in Table S1 in the Supplementary Material. In order to meet *n*-heptane losses lower than 1 % and reducing objective function, the best approach is to set *n*-heptane recovery in the top of the stripping column equal to 75% and, in the distillation column, the reflux ratio in 1 and pyrrole recovery in the distillate stream of 40%. This allows achieving a specific energy demand of 0.170 kWh/kg.

4. Conclusions

Liquid fuel standards are a current discussion in the industry, standing benzene, and N- and S- containing aromatics as an environmental problem. The emergence of cyclic carbonate structure as potential designer solvents derived from CO₂ stands out as a sustainable alternative to explore. In this work, eight cyclic carbonates have been evaluated following a multiscale strategy based on COSMO models. The favorable interaction of cyclic carbonates and aromatics, displaying high values of aromatic/*n*-heptane selectivities, support the conceptual design of a dearomatization process. Before process scale research, the proposal is validated experimentally through a multicomponent liquid–liquid extraction test for Pro-C benchmark solvent, being COSMO-SAC a suitable model.

Results at process scale have demonstrated that several cyclic carbonates show competitive S/F ratios and energy consumption, whereas solvent losses are compatible with the final use of the gasoline and can

be controlled by manipulating the process configuration. From all solvents, Pro-C displays the less specific energy consumption, but Eth-C, But-C and Sty-C are also competitive and with an enhanced behavior in comparison with sulfolane, used as a benchmark in this work. Finally, the compatibility of Pro-C losses in the liquid fuel as a quality enhancer rather than an impurity imposes a truly clean strategy to adjust aromatic content in liquid fuels.

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CRediT authorship contribution statement

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

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.fuel.2022.124005>.

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