An overview process analysis of the aromatic-aliphatic separation by liquid–liquid extraction with ionic liquids

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ABSTRACT

There is a lack of knowledge on comprehensive studies when dealing with ionic liquids and extraction processes. In this work, the computational COSMO-based/Aspen multiscale methodology is applied to perform a comprehensive process analysis over a wide set of 100 common ILs after properly validating against all reliable data published, in the representative field of the aromatic/aliphatic separation. The analysis describes: i) the evolution from extractive properties to extractor behavior; ii) the influence of the rigor of the model -binary (*n*-heptane + toluene) or multicomponent (pyrolysis gasoline) and the process description, namely extractor or complete process with recycling streams; iii) the role of the IL at commercial specifications; iv) the role of the separation train. Main results highlight: i) leading role of mass-based distribution ratio to reduce energy consumption to assess a commercial recovery; ii) selecting an IL with a minimum selectivity required within the more efficient separation train to achieve specifications at the lower energy consumption. Therefore, this work presented a clear guide to properly select the IL extractive properties at process scale and commercial specifications, together with the development of an efficient separation train, as the best approach.

1. Introduction

Benzene, toluene, ethylbenzene, and mixed xylenes, frequently identified by the BTEX acronym, stand as essential compounds in the petrochemical industry. Their uses range from raw materials in the synthesis of intermediate products, i.e., phenol, cyclohexane, and styrene, to final products such as rubbers, lubricants, pesticides, plastics, or paints, among others [1–4]. More than strategic compounds involved in relevant chemical engineering processes, aromatics are currently a growing market, making an opportunity the development of more efficient processes related to aromatics that would be able to fulfill incoming environmental and security standards [4,5].

The availability of aromatics is mostly provided by their isolation from pyrolysis and reformer gasolines, which stand nowadays as their main sources [1]. These petrochemical streams are composed of aromatic and non-aromatic hydrocarbons, being the former in mass concentrations ranging 50–66 wt%. In fact, among other approaches, Sulfolane process remains as the most-used technology for their

separation, covering the wide majority of the aromatic demand all over the world [1,3].

To enhance the aromatic market, the scientific community has made costly efforts for searching substitutes that can replace the most currently used solvent, i.e. sulfolane. Among other alternatives, ionic liquids (ILs) have been and are arguably the most promising alternatives for that purpose. ILs can simplify and improve the conceptual process design due to their special features, namely negligible volatility and designer solvent character, but chiefly enhancing sulfolane standards through relevantly greater aromatic/aliphatic selectivity and comparable or even higher aromatic distribution ratios [6]. Since Meindersma et al. [7] critically collected the first results published in 2005, previously pointed by Huddleston et al. and Letcher et al. [8–11], several achievements have been reported up to the date, mainly dealing with ILs composed by imidazolium and pyridinium-based cations because of their aromaticity. Some tetrafluoroborate ([BF$_4$]) and sulfate ([SO$_4$])-based ILs were initially reported with toluene/*n*-heptane selectivities over that for sulfolane due to the more specific interaction between

these ILs and toluene, discarding other species because of their low potential [12–18]. The first conclusions drawn were: i) [SO$_4$]-based anions provide higher selectivity than [BF$_4$] ones; ii) pyridinium cations provide greater selectivity than imidazolium ones; iii) selectivity decreases as the alkyl chain length of the cation substituents increases. In 2010, Meindersma et al. [19] put forward effective conclusions on the more suitable ILs to separate aromatics from aliphatics with a well-selected IL screening, which remains relevant nowadays. Essentially, Meindersma and coworkers followed the next criteria: i) to report mass-based distribution ratios (avoiding an undesirable molecular weight impact on the results knowing the high values referring to ILs); ii) to select low-viscosity ILs; iii) to avoid selecting ILs with chemical instability or corrosiveness. These criteria narrowed down the ILs to those composed by anions integrated by cyano groups, namely thiocyanate ([SCN]), dicyanamide ([DCN]), tricyanomethanide ([TCM]), and tetracyanoborate ([B(CN)$_4$]). The extractive and physical properties of these ILs have provided the required arguments to evaluate the real feasibility of the sulfolane replacement by ILs, as reviewed by Meindersma et al. in 2012 [20]. Nonetheless, more recent studies have helped to improve the knowledge of the anion-cation combination to achieve concrete extractive properties, concluding in the governance of the anion. In addition, a higher number of certain functional groups, such as cyano groups, means much lower aromatic/aliphatic selectivities and much higher aromatic distribution ratios. Regarding the cation, pyridinium instead of imidazolium permits only to slightly increase both extractive properties. Finally, a higher alkyl chain length of the cation substituents implies a higher capacity and a lower selectivity [20–26].

Other relevant efforts have been made in the last years to extend the knowledge on the separation of aromatic-aliphatic mixtures by liquid–liquid extraction with ILs. Firstly, it is mandatory to understand the IL regeneration in the complete separation process. Anjan [27] claims that the aromatic/IL separation was easy due to the volatility difference, suggesting a flash distillation unit. By contrast, Meindersma et al. [28] evidenced that only with aromatic/aliphatic selectivity over 440, it is possible to separate aromatics in the extractor addressing commercial purities, which means that more units are needed to fractionate the extract stream. In this sense, the knowledge of vapor–liquid equilibria of {aliphatic + aromatic + IL} [29] is needed for the design of the IL regeneration stage. Therefore, later experimental effort was made to measure isothermal vapor–liquid equilibria for {aliphatic + aromatic + IL} systems [30–40]. In vapor–liquid equilibria, the anion nature completely determines the interaction between the aromatics and the IL, playing the cation a secondary role, as evidenced by experimental and theoretical studies [40]. On the other hand, ILs decompose at relatively low temperature, rarely above 473 K, clearly conditioning the conceptual design of the hydrocarbon recovery and IL regeneration units. Fredlake et al. and Crosthwaite et al. reported comprehensive analyses on the thermal stability of imidazolium and pyridinium ILs by dynamic thermogravimetric analysis (TGA) [41,42], later extended by Mu and Cao [43]. However, other studies have demonstrated that dynamic TGA experiments overestimate (between 373 and 423 K) the IL thermal stability [44–50]. Maximum operation temperatures (MOTs) have been calculated for several ILs, which are mainly conditioned by the nature of the anion [46]. This is confirmed by isothermal TGA.

Several distillation schemes have been proposed in the literature to selectively separate the hydrocarbons and the IL based on scarce experimental VLE data and pioneer COSMO-RS predictions within the thermal stability boundaries of the ILs [51–58]. Among all proposals, a series of flashes together with stripping columns have been found up to the date as the most promising configuration to selectively remove the aliphatic compounds and effectively separate the purified aromatic products from the IL, requiring high vacuum conditions and a reduce number of steps or atmospheric pressure and moderate number of steps, respectively [53,59,60].

Secondly, the evaluation of more realistic streams, pilot plant experiences and process simulations have contributed to the analysis of the suitability of ILs as candidates to replace sulfolane in the aromatic/aliphatic separation. Thus, Larriba et al. [55] and Navarro et al. [53] have experimentally tested streams with six or seven hydrocarbons in extraction and recovery units, respectively, with enhanced extraction performance and slightly lower results in the recovery process, finding greater aromatic distribution ratios and lower aliphatic/aromatic relative volatilities due to the higher solubility and volatility of benzene in comparison with toluene. Meindersma et al. [61] worked in a long-term pilot plant study, finding outstanding reutilization and regeneration conclusions regarding the use of ILs for more than three years in the aromatic extraction using a countercurrent contact disc column. Furthermore, De Riva et al. and Larriba et al. provided meaningful insights on IL solvent performance at process scale using the COSMO-based/Aspen Plus methodology [29,59,62]. Overall, the complete separation process of multicomponent aromatic-aliphatic mixtures was modeled for some ILs, including both extraction and regeneration stages [29,59], performing sensitivity analysis of operating variables and estimating energy consumption.

Summarizing, there are significant contributions but the literature lacks a systematic work that can academically guide step by step development of IL-based liquid–liquid extraction processes and to properly select the IL and the process to provide a more competitive IL-based technology. A priori methodologies stand as the most powerful methodologies to address this limitation of the literature. The integration of molecular and process simulation tools in COSMO-based/Aspen approach [62,63] has been extensively used with success for several IL-based processes in a wide range of applications: CO$_2$ capture [58,64,65], gas separations [66,67] and absorption refrigeration cycles [68,69], taking into account thermodynamic, kinetic, technical and/or economic selection criteria.

In this work, COSMO-based/Aspen methodology is used to overview the role of extractive properties of ILs on the separation performance of aromatic-aliphatic mixtures by liquid–liquid extraction at process scale. A representative sample of 100 common ILs, with markedly different structural features, is included in the current analysis. The predictability of COSMO-based/Aspen methodology was ad hoc validated to liquid–liquid and vapor–liquid equilibria regarding ILs and hydrocarbons as can be found elsewhere [70], thus making it available for this work. The structure of the work responded to the next partial objectives: i) correlate aromatic distribution coefficient and aromatic/aliphatic selectivity with aromatics and aliphatics recoveries and purities; ii) explore the evolution in aromatics and aliphatics recoveries and purities from changes in the refinery stream definition (binary or multicomponent) and the process description (extractor or complete process with recycling streams); iii) find a rule to select the IL at process scale for commercial standards; iv) propose the best IL-separation train pair.

2. Computational details

2.1. Component definition and property model specification in Aspen plus

Most of the ILs selected in this work were incorporated as conventional components using the ILUAM database [62] in Aspen Plus v11 process simulator (100 ILs available to be used in the process simulator). Other ILs with interesting properties to be evaluated in this work ([4mepy][NTf$_2$], [4mbpy][NTf$_2$], [allylmim][DCN], [4mepy][TCM], [4mbpy][TCM] and [bzmim][DCN]) were incorporated into the process simulator using the COSMO-based/Aspen methodology [62,63]. ILs geometries are created as ion pair structures (CA) and independent ions (C + A) [71,72] using Turbomole [73] (TmoleX graphical interface) at BP/TZVP quantum level [74–76] and including COSMO solvation model [77,78]. COSMO-RS method was used with COSMOtherm software [79] to predict the required IL properties (liquid density at 60 °F, normal boiling point, and molecular weight) to be incorporated as pseudo-component in Aspen Plus. In addition, since the COSMO-SAC model [80] is used as property package, the different σ-profile (SGPRF1 to

SGPRF5 properties in Aspen Plus) and the COSMO cavity volume was added (CSACVL parameter) in the pure component properties from COSMO-RS calculations. For the gasoline model, all the information required in the Aspen simulator databases is found, and then the compounds were simply selected.

Experimental data from the ILthermo database [81] were validated for the 6 COSMO-based/Aspen combinations [62]: both IL molecular models ion pair (CA) and independent ions (C + A), in addition to the 3 COSMO-based models available in Aspen Properties (COSMO-SAC [82], COSMO-RS 1995 [83] and Lin & Mathias COSMO-SAC modification [84]). The results suggested that COSMO-SAC and ion-pair molecular model (CA) allowed the best description of the experimental data [70].

2.2. IL extractive properties calculations

The aromatic distribution ratio and toluene-*n*-heptane selectivity calculations (see Eqs. (1) and (2) using mass fractions) of each IL were calculated using a decanter at 313 K (one equilibrium stage) with a solvent / feed ratio (S/F) equal to 1 in mass units. The feed to the decanter was formed by a binary mixture of (*n*-heptane + toluene) with 35 wt% of toluene.

$$\beta = \frac{x_{toluene}^{ionicliquidphase}}{x_{toluene}^{hydrocarbonphase}} \tag{1}$$

$$S = \frac{x_{toluene}^{ionicliquidphase} / x_{toluene}^{hydrocarbonphase}}{x_{n-heptane}^{ionicliquidphase} / x_{n-heptane}^{hydrocarbonphase}} \tag{2}$$

2.3. Extractor simulation

Separation performances (recovery and purity) of aromatic and aliphatic compounds were calculated using an EXTRACT model at 313 K and 1 bar with 5 equilibrium stages. The refinery stream was modelled considering both a binary mixture of (*n*-heptane + toluene) with a mass fraction of 0.34 of *n*-heptane or a multicomponent stream that replicates the composition of a typical pyrolysis gasoline (Table 1).

2.4. Process simulation

2.4.1. Extractor

Separation performance of the extractor alone for binary or multi-component model was computed using the EXTRACT model at 313 K and 5 equilibrium stages, operating with a S/F ratio of 5. The value selected aims to effectively show the role of IL nature on extraction performance.

2.4.2. Complete process: Case A

The extractor (represented by EXTRACT model) operates at 313 K and it is completed with a distillation train that consists of 3 flash distillation units at the conditions, as can be seen in Fig. 1, with the details collected in Table 2. Case A is used with the extractor operating with 5 or 20 stages in the results sections 3.2 or 3.3., respectively, the latter to meet commercial standards. The first two flash distillation units (V-100 and V-101) work at milder temperatures to enhance higher

Table 1
Pyrolysis gasoline compositions adapted from Franck and Stadelhofer [1].

Hydrocarbon	wt. %
n-Hexane	11.3
n-Heptane	11.3
n-Octane	11.3
Benzene	33.8
Toluene	19.3
p-Xylene	13.0

aliphatic/aromatic relative volatilities, selectively removing the aliphatics to improve the aromatic purity in the liquid from V-101. Then, the purified aromatics are recovered from the solvent in a final stage (V-102), where temperature and vacuum are higher aiming at completely separating aromatics and the IL. The selected temperature allows thermal stability of the majority of the ionic liquids but not all; however, the necessity of a benchmark value for comparison purposes and the fact that best ionic liquids met the criteria support this approach. FLASH2 model was used to simulate each flash distillation unit. The refinery stream was modelled considering both a binary mixture of (*n*-heptane + toluene) with a mass fraction of 0.34 of *n*-heptane or a multicomponent stream that replicates the composition of a typical pyrolysis gasoline (Table 1).

Utility costs were calculated from the energy duties of each equipment. A year was taken as a basis for calculation (8000 h of operation). The prices of the utilities that appear by default in the Aspen Plus v9 simulator were taken as reference (Table 3).

2.4.3. Complete process: Case B

The extractor T-100 (20 stages and represented by EXTRACT model) operates at 313 K and it is completed with a distillation train that consists of 2 stripping columns (T-101 and T-102) and a flash distillation unit (V-100), as shown in Fig. 2 and at the conditions collected in Table 4. First stripping column aims to purify the aromatics in the liquid by distillation, selectively removing the aliphatics due to the high aliphatic/aromatic relative volatility in the extract stream together with a multistage device; in comparison with V-100 and V-101 from Case A, the stripping column T-101 is demonstrated to be more efficient since the aliphatics recovered are more pure [60]. The second stripping column, T-102, aims to regenerate the IL up to 0.995 mass fraction purity in the liquid. The use of N_2 instead of generating a vapor stream in the reboiler was demonstrated to be efficient in terms of energy consumption and allows avoiding the use of vacuum due to the well-known thermal stability limitation associated to ionic liquids [60]. Final flash distillation unit, V-100, separates the condensed aromatics from the N_2 gas. Utility costs were calculated from the energy duties of each equipment analogously to Case A.

3. Results

3.1. Property-solvent relationship and extractor performance vs extractive properties

Fig. 3 (see more details in table S3 in the Supplementary Material) presents the calculated toluene/*n*-heptane selectivity (S) and toluene distribution ratio (β) between extract and raffinate phases for the ILs (83 ILs exhibits immiscibility with the hydrocarbon mixture) studied in this work. As expected, it is observed a wide range of solvent behaviors depending on the IL structure within an inverse coupled trend of both extractive properties. It is not possible to maximize the two extractive properties at the same time, thus imposing a difficult challenge to select an IL. Four well-known ILs in the field are highlighted to ease the evaluation of the results for a representative and reduced number of solvents for this study and considering literature findings.

Regarding high toluene/*n*-heptane selectivity and low toluene distribution ratio, [emim][SCN] was firstly selected. Sulfate-based ILs were initially proposed and provided similar results in terms of selectivity [85–88]; however, they are thermally unstable at temperatures required in the regeneration of the solvents [43,44,49]. Later works showed that ILs with thiocyanate anion, [SCN], provide the maximum toluene/*n*-heptane selectivity reported up to the date [6,20,25] and show lower viscosities than those for sulfate-based ILs [49]; therefore, [emim][SCN] has been reported as favorable extracting solvent for aromatic-aliphatic separation. On the other hand, the wide majority of ILs are in a region characterized by both extractive properties achieving intermediate values (Fig. 3). Thus, two ILs have been selected to properly represent
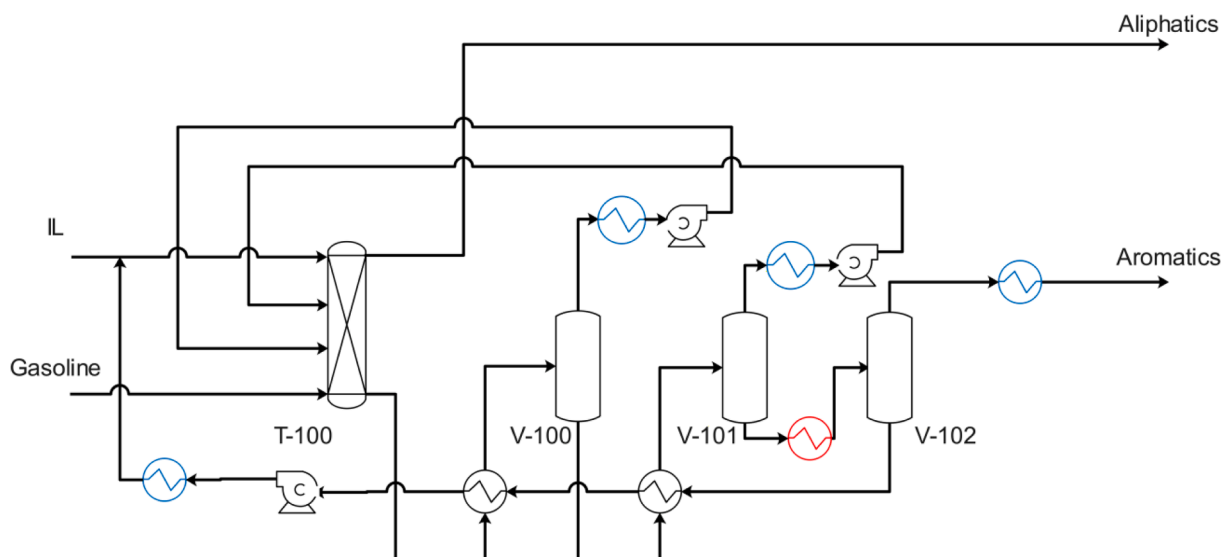
Fig. 1. Simplified flow diagram of Case A. The allocation of heating or cooling in the process is highlighted in red or blue, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 2
Pressure and temperatures of the separation train in Case A.

Equipment	V-100	V-101	V-102
T (K)	333	333	393
Pressure (bar)	0.3	0.2	0.01

Table 3
Prices used in this work for the utilities.

Utility	Cooling water	HP steam	Electricity
Price	$2,12 \cdot 10^{-7}$ \$/kJ	$2,5 \cdot 10^{-6}$ \$/kJ	0,0775 \$/kWh

this kind of solvents. The IL [allylmim][DCN] was selected as a solvent with slightly lower selectivity than [emim][SCN] but moderately increasing the toluene distribution ratio, in good agreement with experimental evidences [24]. The IL [allylmim][DCN] was preferred over other IL families that provide similar extractive properties, such as tetrafluoroborate-based ILs, but considerably increasing the viscosity and the chemical instability, especially with water [14,89,90]. In

Table 4
Pressure and temperatures of the separation train in Case B.

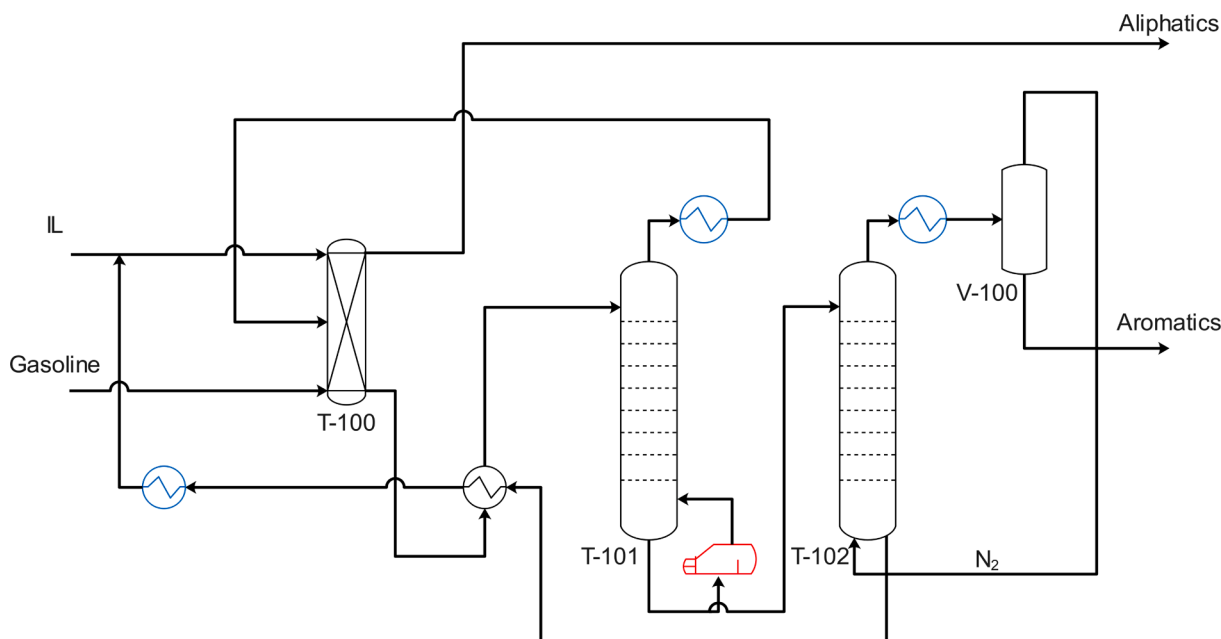| Equipment	T-101	T-102	V-100
T (K)	–	–	298
Pressure (bar)	1	1	1
N stages	5	3	–

Fig. 2. Simplified flow diagram of Case B. The allocation of heating or cooling in the process is highlighted in red or blue, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
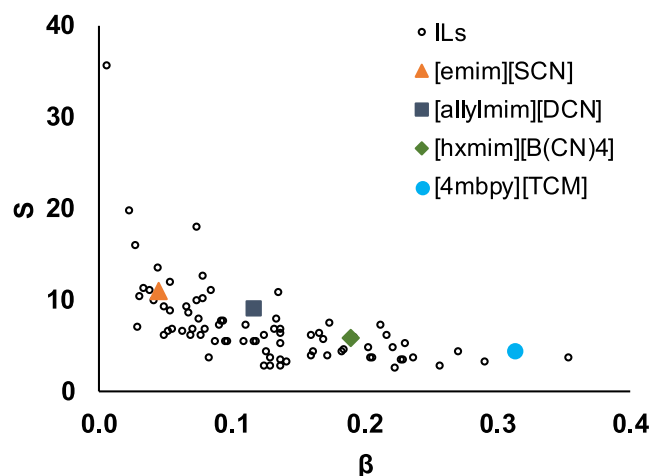
Fig. 3. Toluene/*n*-heptane selectivity (S) and toluene distribution ratio (β) (in mass unit) between extract and raffinate phases for the ILs studied in this work for a single equilibrium liquid–liquid extraction with a S/F = 1 in mass basis at 313 K using a binary mixture of (*n*-heptane + toluene) with a mass fraction of 0.34 of *n*-heptane.

addition, [hxmim][B(CN)₄] was chosen to represent moderate-high toluene distribution ratios and medium–low selectivity [20]. Experimental previous studied reported tetracyanoborate-based ILs as enhanced solvents for toluene/*n*-heptane separation, when compared with other ILs with similar extractive properties, namely hexafluorophosphate-based ILs, due to the viscosity and chemical stability issues [89,91]. Finally, [4mbpy][TCM] was proposed to represent IL solvent with high toluene distribution ratio and low toluene/*n*-heptane selectivity ILs, since this IL showed the greatest experimental toluene distribution ratio value reported so far [26,92–95]. Other ILs, as those based on bis(trifluoromethylsulfonyl)imide (NTf₂) anion, present high toluene distribution ratios with moderate viscosities and high thermal stability [92–95]; however, aiming at selecting the most potential solvents from an industrial point of view, [4mbpy][TCM] shows enhanced capacities with lower viscosity and very close thermal stability in comparison with NTf₂-based ILs. In sum, selected ILs composed by cyano-based anions (namely thiocyanate, dicyanamide, tricyanomethanide and tetracyanoborate) clearly exemplify the trend shown in Fig. 3 and agree with the recommendations from literature, being proposed as promising candidates in the field.

Next step is evaluating the role of IL in aromatic-aliphatic separation by liquid–liquid extraction using a countercurrent extraction column (N

stages = 5, S/F ratio = 5). Fig. 4A presents the achieved recovery and purity of *n*-heptane in raffinate stream, whereas Fig. 4B compares the obtained toluene recovery and purity in extract stream for all the studied ILs; highlighting the four ILs previously selected. As can be seen, the different extractive properties of the studied ILs allowed covering the whole range of separation efficiencies in extraction unit: i) from nearly to 0 to 100% recovery of aromatic or aliphatic compounds; and ii) from 65 to 100% of toluene purity in extract phase and 35 to 100% of *n*-heptane purity in raffinate phase. It is clearly observed that increases the aromatic recovery means decreases the purity of this compound in the extract stream (Fig. 4B). The same is observed respect to aliphatic compound in raffinate stream (Fig. 4A). In addition, it was found a reverse coupling between *n*-heptane and toluene recoveries, as expected, because of the relationship between the extractive properties; *i. e.* ILs with high selectivity (S), as [emim][SCN], allow obtaining high aliphatic recovery in raffinate phase and high aromatic purity in extract phase, whereas ILs with high distribution ratio (β), as [4mbpy][TCM], provide high aromatic recovery and high aliphatic purity in the extraction column.

Moreover, Fig. 5 shows a clear linkage between aromatic recovery and aliphatic purity and vice versa; *i.e,* one can select the IL extracting solvent to efficiently recover the aromatic compound (obtaining aliphatic product of high quality, see [4mbpy][TCM]) or to increase the purity of aromatic product (obtaining low losses of aliphatic compound, see [emim][SCN]), transferring the challenge of extractive properties to the extractor design.

A final picture about the dependence between extractive properties and process performance of ILs in the extraction unit is revealed by Fig. 6 (see also Figure S1 in the Supplementary Material). The results are clearly conditioned to the case study (i.e. fixed number of stages and S/F ratio and the absence of separation train and recycling streams) but illustrates that there are cases at which increasing the extractive properties does not mean an improvement in the separation performance (the extractor maximizes recovery with distribution coefficients of around 0.2 and the purity is almost constant with selectivities above 15).

Toluene recovery in the extract phase is well-described by the toluene distribution ratio (β) for the whole sample of studied ILs (Fig. 6A); the linear relationship and the low dispersion of the trend is clearly justified by the toluene recovery independency from the *n*-heptane distribution ratio and, thus, from the toluene/*n*-heptane selectivity; thus, ILs with high aromatic distribution ratio, as [4mbpy][TCM], allow obtaining 100% of aromatic recovery in current operating conditions, whereas those ILs with opposite extractive properties, as [emim][SCN], only recover 25% of toluene.

On the other hand, if one focuses on the aromatic purity dependence on the toluene/*n*-heptane selectivity, a more complex analysis should be
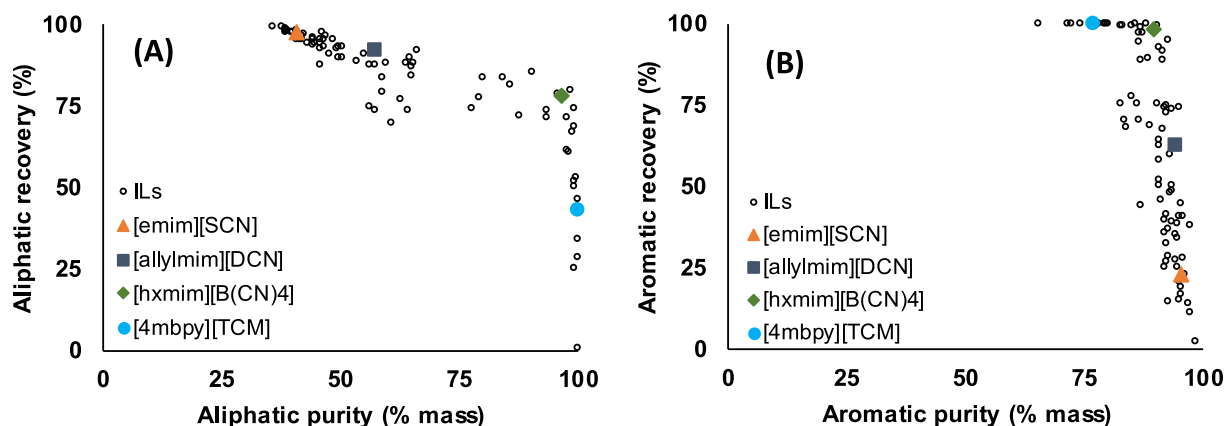

Fig. 4. Recoveries and purities from the liquid–liquid extraction in a countercurrent extraction column (N = 5, S/F = 5) a binary mixture of (*n*-heptane + toluene) with a mass fraction of 0.34 of *n*-heptane. Relationship between different stream properties: (A) Trend of the aliphatic recovery vs aliphatic purity in raffinate phase (B) Behavior of the aromatic recovery vs aromatic purity in extract phase.
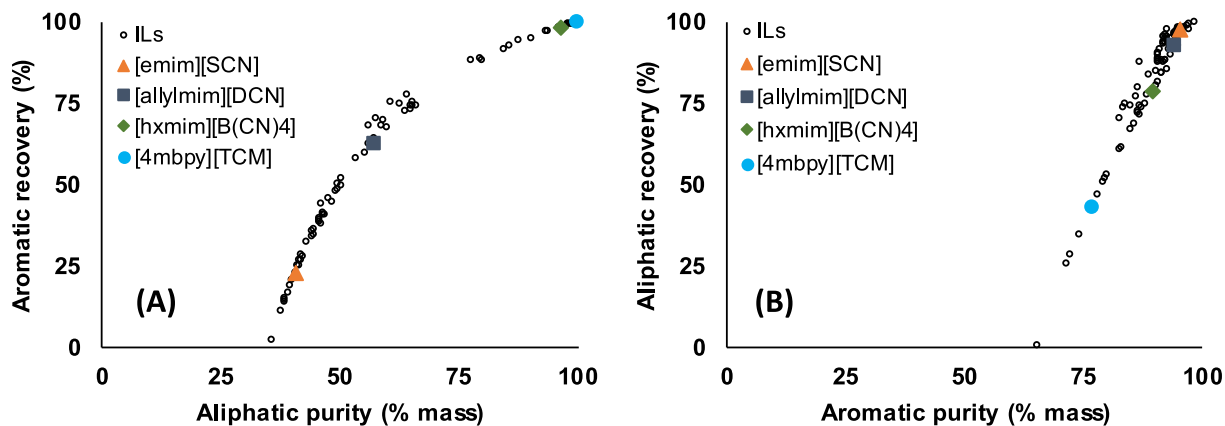
Fig. 5. Recoveries and purities of the liquid–liquid extraction in a countercurrent extraction column (N = 5, S/F = 5) using a binary mixture of (n-heptane + toluene) with a mass fraction of 0.34 of n-heptane. Relationship between different stream properties: (A) Correlation of the aromatic recovery and aliphatic purity (B) Linear connection of the aliphatic recovery and aromatic purity.
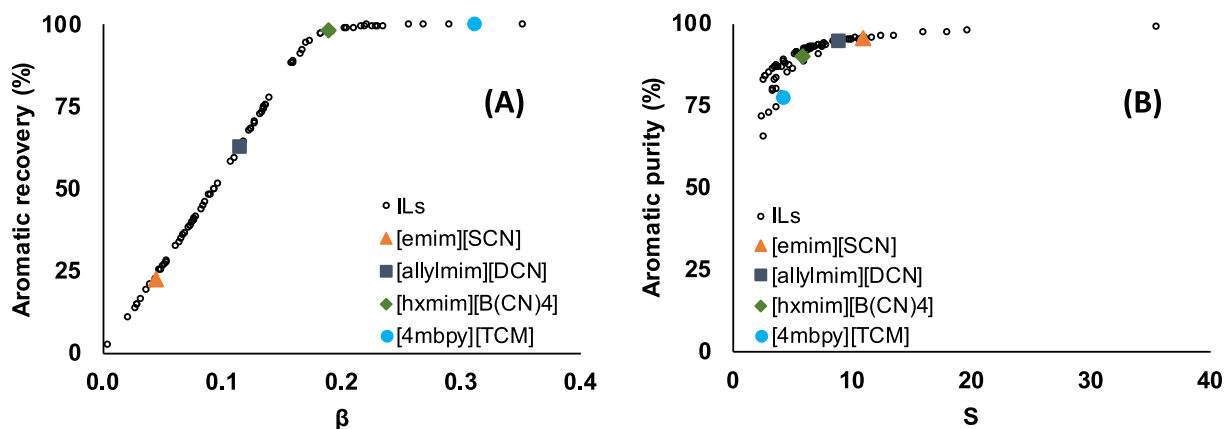

Fig. 6. Relationships between (A) the aromatic recovery in extraction unit and the aromatic distribution ratio (β) of the IL; and (B) the aromatic purity in extraction unit and the toluene/n-heptane selectivity (S) of the IL. Recoveries and purities obtained using a countercurrent extraction column (N = 5, S/F = 5) using a binary mixture of (n-heptane + toluene) with a mass fraction of 0.34 of n-heptane.

done. Fig. 6**B** shows an asymptotic curve when comparing toluene purity and toluene/n-heptane selectivity of IL, with slight dispersion. Toluene/n-heptane selectivity is calculated by the distribution ratios of both hydrocarbons. Therefore, although it is clear that higher toluene/n-heptane selectivity lead to achieve enhanced toluene purities, low fix values of selectivity are found related to different hydrocarbons distribution ratios. Thus ILs with similar low values of toluene/n-heptane selectivity, as [hxmim][B(CN)$_4$] and [4mbpy][TCM], present remarkably different aromatic purity (75 and 90%). It is explained because, when aliphatic hydrocarbons distribution ratios are high, small changes in their values can provoke significant variations in the toluene purity due to the n-heptane mass fraction variations in the extract stream. On the other hand, for highly selective ILs, as [emim][SCN] or [allylmim] [DCN], a clean relationship between the high toluene purity and toluene/n-heptane selectivity is found (Fig. 6**B**), expected behavior since low distribution ratios of aliphatic hydrocarbons imply that their composition in extract phase is almost negligible. Relating these results with literature, the trends obtained agree with previous computational evidences in the literature: Larriba et al [55,96] have reported high aromatic recoveries and high aliphatic purities when using ILs with high aromatic distribution ratio, namely [emim]$_2$[Co(SCN)$_4$] and [4mepy] [NTf$_2$], whereas Navarro et al. [56] Larriba et al. [96] and de Riva et al. [29] also reported high aromatic purities and aliphatic recoveries by using high selective ILs, such as [emim][SCN], [emim][DCN] and [4mbpy][BF$_4$].

3.2. The role of the complexity of the model: Impacts of refinery stream model and the process description

Four scenarios are evaluated to understand how the refinery stream model (from binary to six-compounds multicomponent model) or the process definition (stand-alone extractor or the complete process described in the methodology as Case A) impact on the aromatic recoveries and purities.

As can be seen in Fig. 7, the aromatic recovery in the extraction column is comparatively higher for the multicomponent than for binary mixture. This easily attributed to the higher distribution ratio of benzene than that of toluene in ILs [55] and the higher benzene concentrations in comparison with toluene and p-xylene, so the lighter the aromatic, the higher the distribution ratio and the recovery in the extract. In the complete process, the composition of treated mixture clearly affects the aromatic recovery when using ILs with low extraction capacity (as [emim][SCN]). The higher volatility of benzene, compared to toluene, explained the loss of aromatics in the complete process, particularly in the case of ILs with low chemical affinity for aromatic (low β values). Regarding selectivity, the distillation train clearly allows obtaining an aromatic product with higher purity for multicomponent approach, being this effect more evident when using ILs with high extractive capacity, as [4mbpy][TCM]. This enhancement of aromatic purity in the complete process when separating the pyrolysis gasoline model is related to high volatility of n-hexane compound, which is efficiently
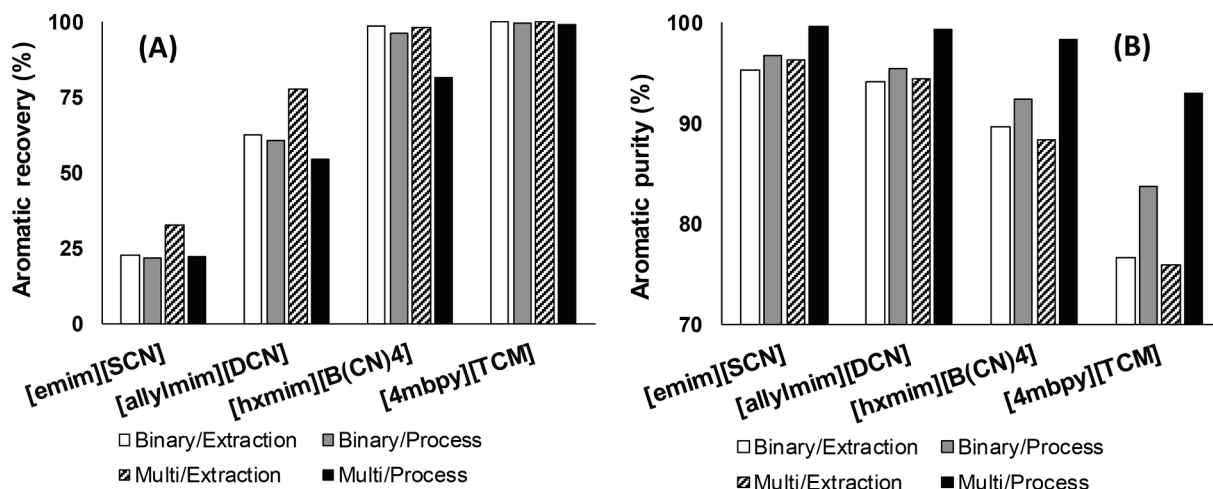
Fig. 7. Comparison of the aromatic (A) recovery and (B) purity as function of process description (extraction unit/complete process) and the refinery stream model (binary/multicomponent). In all cases, a countercurrent extraction column with N = 5 and S/F = 5 is used.

removed from extract phase in the first and second flash units (Case A). Certain studies in the literature deal with different refinery streams, i.e. reformer and pyrolysis gasolines, which have different contents of aromatics, especially of benzene. Larriba et al. [55] reported the improvement of both aromatic recovery and purity in the extract stream when the benzene concentration in the feed increases. According to this, Navarro et al. [53] also discussed the negative impact of benzene on the aromatic recovery in the distillations train due to their high vapor pressure. In any case, the difficulty for efficiently recovering the aromatic product with high purity remains whatever the extracting solvent, treated mixture or the process configuration.

A first look into the utility costs (heating, cooling and electricity) is depicted in Fig. 8 using the 4 selected ILs. As observed, energy consumption surprisingly increases as the distribution ratio of the IL does because of the higher aromatics recovery; however, the specific energy consumption is improved, as expected, with the aromatic distribution ratio. Although this picture is not of interest for design purposes, it is representative of two main points: i) the relevance of comparing solvents for the same separation problem and ii) the preferably use of specific energy consumption rather than energy consumption.

The effect of S/F ratio combined with the nature of the IL is shown in Fig. 9 to further explore these two points. First, varying S/F ratio within reasonable values (1 to 10), one can tune the process to address comparable aromatics purity or recoveries (see Fig. 9A and 9B) or evidence that the IL is inefficient due to low values of aromatic distribution coefficients ([emim][SCN]) or aromatic/aliphatic selectivities ([4mbpy]

[TCM]). As can be observed, aromatic recovery increases with S/F value (Fig. 9A) up to reach an optimum value with nearly 100% of aromatic recovery; later increase of S/F is inefficient. The optimum S/F ratio is different for each IL, decreasing for higher aromatic distribution ratio. In Fig. 9B is observed that aromatic purity remains nearly constant up to optimum S/F value, then starting to decrease. It is well-documented that S/F determines both separation effectiveness and operating costs [29,52,59], but reasonable values at process scale can evidence ILs to be discarded. Regarding energy consumption (Fig. 9C), clearly it mainly depends on the IL flow, but also on the hydrocarbon extracted, observing a decreasing of the trend slope for S/P ratios over its optimum. Fig. 9D shows that specific energy demand remains nearly constant with S/F ratio, slightly increasing over the optimum S/F, since the solvent is partially destined to extract undesirable aliphatics. This scenario clearly states that fix a S/F ratio to compare several ILs is not recommended at all. Centering the attention in the [4mbpy][TCM] case, working over the optimum S/F implies deteriorating the aromatic purity and unnecessarily increasing the energy consumption, not fairly evaluating this IL if we arbitrary fix an overestimated S/F.

3.3. The impact of the specifications in aromatic recovery and purity in the IL selection

Fig. 10 comprises the results when aromatic recovery is specified to 99% of aromatic extraction and S/F ratio is varied for each IL to achieve this separation specification. As can be seen, the higher the distribution
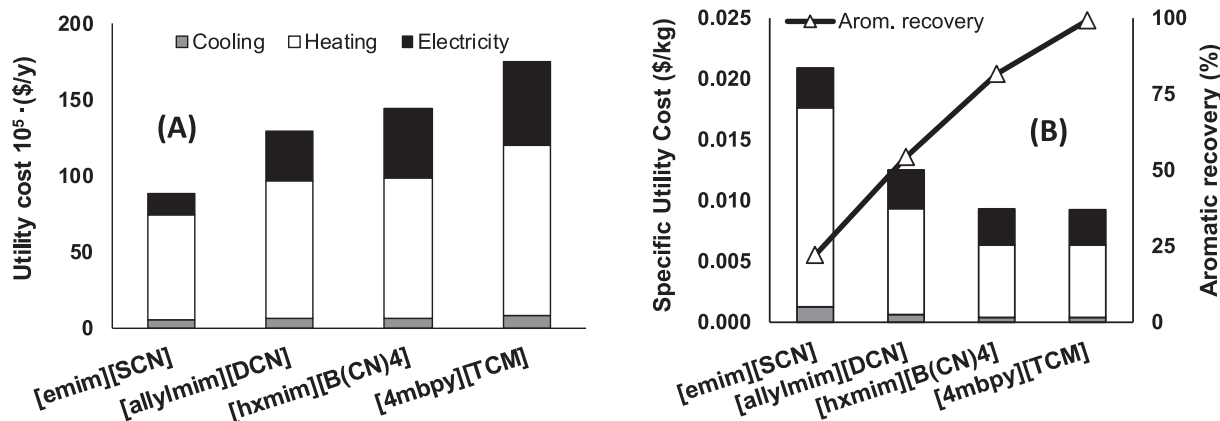

Fig. 8. (A). Utility costs and (B) Specific utility cost (defined per mass unit of aromatic recovered) of the complete separation process calculated for the 4 selected ILs. In all cases, a countercurrent extraction column with N = 5 and S/F = 5 is used to separate the multicomponent refinery stream described in Table 1.
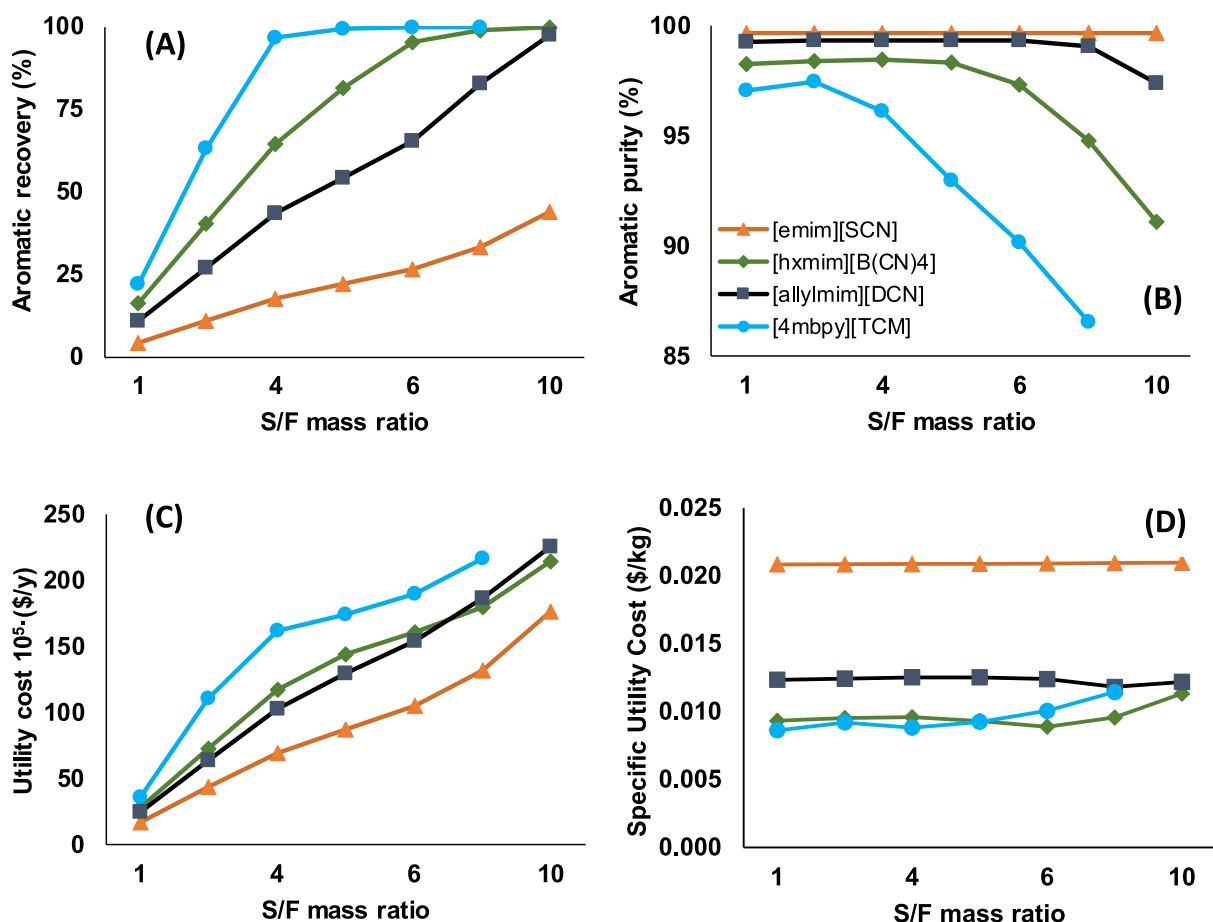
Fig. 9. Dependence of the (A) aromatic recovery, (B) aromatic purity, (C) utility costs and specific aromatic utility costs (D) dependence with the solvent/feed (S/F) ratio using a countercurrent extraction column (N = 5) for separating the multicomponent refinery stream described in Table 1.
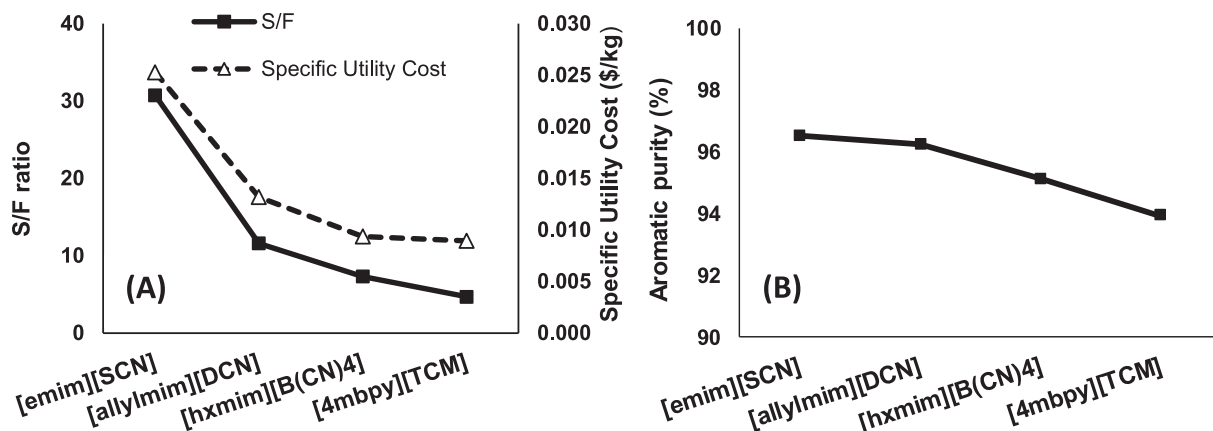

Fig. 10. S/F ratio and utility costs (A) and (B) Aromatic purity as a function of the IL calculated for a specification of aromatic recovery of 99 using a countercurrent extraction column (N = 5) for separating the the multicomponent refinery stream described in Table 1.

ratio, the lower the solvent consumption and the energy consumption; however, aromatic purity is deteriorated when using an IL with higher aromatic distribution ratio since it is coupled to a lower aromatic/aliphatic selectivity. Since the industrial aromatic extraction requires high recoveries and purities in the process, results reported in Fig. 10 are insufficient to select an IL.

To simultaneously satisfy both separation specifications, 99 % of aromatics recovery and 99 wt% of aromatics, S/F ratio was the adjustable variable and the temperature in flash distillation units 1 and 2

(**Case A**) were increased to 353 K. Among the 4 selected ILs, only those with higher aromatic/aliphatic selectivity ([emim][SCN] and [allylmim][DCN]) allow achieving both specifications. In fact, analyzing the 83 ILs of Fig. 3, it was possible to find few ILs that permit to achieve both specifications, but always with a selectivity value over a minimum one related to the purity specification (see horizontal dashed line of Fig. 11A). Hence, it can be concluded that it is necessary to select an IL solvent with a minimum selectivity (S_{min}) for assessing certain aromatic purity specification for current process configuration. Once purity
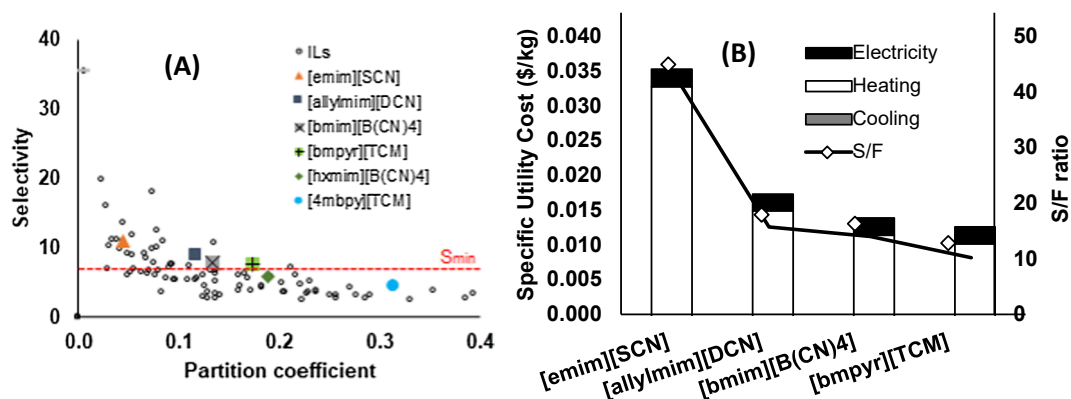
Fig. 11. (A). Selectivity and distribution ratio calculated for a single equilibrium stage and the minimum selectivity calculated to achieve the 99% of aromatic purity and recovery in the complete process. (B) S/F ratio and utilities cost calculated to obtain a 99% recovery and 99% purity of aromatic product in the complete separation process, using a countercurrent extraction column (N = 20) for separating the multicomponent refinery stream described in Table 1.

specification is achieved, moving through the horizontal line of S_{min} toward higher distribution ratio (β) values, it is possible to minimize the solvent consumption and, thus, the utility costs (Fig. 11B). It contrasts with the common strategy in bibliography of designing ILs with improved selectivity and extraction capacity, evidenced by Canales and Brennecke in their review on the topic [6]. Therefore, the performed comprehensive process analysis provides a guide for the design of effective IL solvents (or mixtures involving ILs) to separate aromatic compounds from gasolines by liquid–liquid extraction, focused on fulfilling product quality standards and minimizing solvent consume and energy duty.

3.4. Process redesign and IL selection

Case A process configuration has shown clear limitations to fulfill commercial specifications named aromatic recovery of 99 % together with 99 wt% of mass purity of the extracted aromatics. Best approach was the use of [bmpyr][TCM] solvent, but S/F ratio is high to be competitive in terms of energy consumption. Case B emerges as a more efficient separation train because the first stripping column reduces the aromatic recycled to the extractor and, thus, the S/F ratio and the energy consumption, as reported in the literature [60]. In addition, the use of a stripping agent, N_2, in the second stripping column avoids the vacuum costs and limits the heating requirements [60]. Therefore, Case B scheme is evaluated using [bmpyr][TCM], [4mbpy][TCM] and [N_{2225}][NTf$_2$] ionic liquids, since [bmpyr][TCM] is the best candidate in Case A, [4mbpy][TCM] is the reference one with largest aromatic distribution ratio considering literature trends, and [N_{2225}][NTf$_2$] is the IL with the largest aromatic distribution ratio predicted by COSMOSAC model. The results in terms of specific energy consumption are displayed in Fig. 12 together with the required S/F ratio.

As can be seen, a more efficient separation train allow reducing energy demands about one magnitude order as well as eliminating the vacuum requirement. Case A is simpler but has a higher energy demand, whereas Case B optimizes utility costs and solvents consumption with a more complex flow diagram. Therefore, it is demonstrated by process simulation that it is more efficient to deal with a high-capacity IL within the selectivity limits of a separation train and, thus, the improvement of the separation train is the key to allow reducing utility costs. In fact, the two ILs displaying the highest distribution ratios are the best candidates in terms of energy consumption. [4mbpy][TCM] is one of the most studied ILs in the specific literature and here its use is justified at process scale, whereas [N_{2225}][NTf$_2$] emerges as a novel structure, optimized at process scale and feasible in terms of synthesis and with reasonable thermophysical properties [97], which can reopen the search of more efficient ionic liquid-based systems to separate aromatics and aliphatics. Of course, the specific findings are based on COSMOSAC predictions,
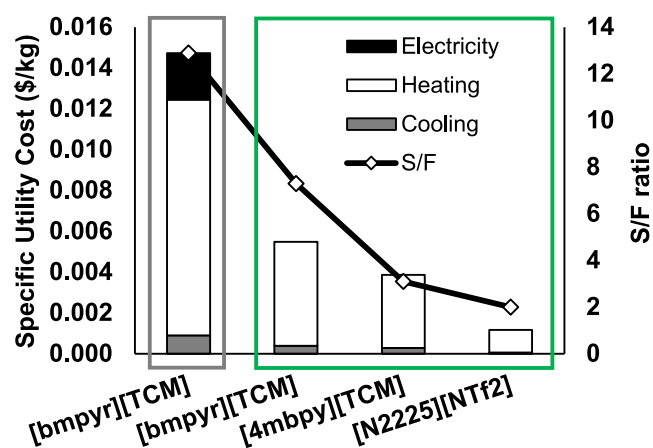

Fig. 12. Specific energy consumption and S/F ratios for selected ILs within Case B (green box) against benchmark results from Case A (grey box) using [bmpyr][TCM] ionic liquid, using a countercurrent extraction column (N = 20) for separating the multicomponent refinery stream described in Table 1.

which demand a next step consisting in *ad hoc* experimental validation for each promising candidate. It should be noted that COSMOSAC tends to underestimate the behavior of ILs, as in the case of high effective TCM-based ILs [70], so the potential of ILs could be even greater in the aromatic/aliphatic separation.

4. Conclusions

Taking advance of a representative sample of 100 common ILs with markedly different structural features and using COSMO-based/Aspen methodology, an overview analysis has been executed to evaluate the impact of ILs on the aliphatic/aromatic separation by liquid–liquid extraction from a process point of view.

First, the relationship between extractive properties (distribution ratio and selectivity) of the ILs have been correlated to the recoveries and purities in the outcome streams of the extractor selecting four representative ILs in terms of distribution ratio and selectivity values for monitoring the key process indicators.

Second, the recovery and regeneration units, the composition of the refinery stream and the S/F ratio have been evaluated and analyzed for the selected ILs, finding their impacts on the separation effectiveness and the operating costs, namely heating, cooling and vacuum consumptions. Those ILs that exhibit higher distribution ratios required less S/F ratios, which implied lower operating costs per unit of aromatic recovery.

Finally, the complete process has been designed for commercial standards, namely aromatic recovery of 99 % and aromatic purity of 99 wt%. It has been found that there is a minimum selectivity required to address the desirable separation for the separation train based on three flash distillation units, whereas the aromatic distribution coefficient is the optimization parameter to reduce operating costs among the ionic liquids reaching the selectivity required. In that context, the redesign of the separation train from using flash distillation units to use stripping columns is revealed as the main aspect of the process, since a more efficient separation train allows working with the IL with the highest distribution coefficient, $[N_{2225}][NTf_2]$, imposing a reduction of specific utility cost from 0.015 to 0.0015 \$/kg, with significant low S/F mass ratio (2) and avoiding the requirement of vacuum.

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Pablo Navarro: Conceptualization, Data curation, Formal analysis, Investigation, Writing – original draft. **Daniel Moreno:** Data curation, Formal analysis, Investigation, Writing – original draft. **Marcos Larriba:** Formal analysis, Investigation, Writing – review & editing. **Julián García:** Formal analysis, Investigation, Writing – review & editing. **Francisco Rodríguez:** Funding acquisition, Project administration, Writing – review & editing. **Roberto I. Canales:** Formal analysis, Investigation, Writing – review & editing. **José Palomar:** Conceptualization, Funding acquisition, Project administration, Resources, Software, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.seppur.2023.123848.

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