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This is an **author produced version** of a paper published in:

Industrial & Engineering Chemistry Research 58.44 (2019): 20370-20380

DOI: <https://doi.org/10.1021/acs.iecr.9b04603>

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Stripping Columns to Regenerate Ionic Liquids and Selectively Recover Hydrocarbons Avoiding Vacuum Conditions

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Abstract

There is a large number of liquid-liquid extraction processes where ionic liquids (ILs) are proposed as solvents. However, the development of the purification and IL regeneration units still represents a challenge. Several effective separation trains were proposed to regenerate ILs, but extreme vacuum is needed to achieve commercial standards, which demands extra energy and extra solvent consumptions due to recycling streams. In this proposal, the use of stripping columns stands as a promising IL regeneration technology to avoid vacuum conditions and to enhance the separation of the compounds that form the extract stream, explored in the aromatic-aliphatic separation. COSMO-based/Aspen Plus methodology is applied to extensively evaluate the role of the IL nature and easily evaluate the influence of the main operating variables, namely temperature feed, column pressure, reboiler heat, number of stages on the separation efficiency. A critical comparison between current proposal and the benchmark IL regeneration process is reported, analyzing the aromatic recovery, energy duty and operating cost. The use of two stripping columns for the IL regeneration stage evidences the potential of this new configuration, drawing a new paradigm in which mild conditions are enough to conceptual design new separation processes involving ILs.

Keywords: Ionic liquids; aromatic/aliphatic separation; stripping columns; COSMO-RS; Aspen Plus

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1. Introduction

ILs are non-conventional salts that are liquid below 100 °C, showing negligible vapor pressure and reasonably good thermal stabilities¹⁻³. This interesting liquid range has motivated the extensive use of ILs for separation purposes, mainly as solvents in liquid-liquid extraction processes⁴⁻¹⁴. Among other potential application, a noticeable research effort has been deployed regarding the aromatic/aliphatic separation¹⁵⁻²⁶. Many ILs have shown attractive and higher aromatic/aliphatic selectivity than those obtained by conventional industrial solvents²⁷⁻³⁰, such as sulfolane, whereas, although scarce, some ILs have shown also better mass-based aromatic distribution ratios than that of sulfolane^{31,32}; thus, evidencing better extractive properties than those at which Sulfolane process operates. Nevertheless, despite the fact that non-volatile character of ILs was advised as its main advantage³³, the design of the hydrocarbon recovery section together with the IL regeneration was revealed as the limiting task³⁴⁻³⁸. The aromatics are extracted with a purity below commercial standards, which is not avoidable by tuning the solvent. In fact, according to Meindersma³⁹, only an IL with an unrealistic toluene/*n*-heptane selectivity of 440 could avoid additional purifications. Therefore, the feasibility of this liquid-liquid extraction process is fully dependent on the recovery section design, pointing extractive distillation configuration as an enhancer technology⁴⁰.

A first drawback found by the research community regarding IL regeneration stage was finding reliable vapor-liquid equilibria (VLE) data regarding extract stream conditions. Because of the high IL concentration, this phase equilibria determination implies mixing problems in dynamic and isobaric techniques, concluding that static and isothermal determinations are preferred⁴¹. The scarce data collection available up to date comprises isothermal VLE imidazolium and pyridinium-based ILs integrated by cyano-based anions, namely thiocyanate, dicyanamide and tricyanomethanide, tetrathiocyanatocobaltate and bis(trifluoromethylsulfonyl)imide one^{31,32,41-48}.

The next problematic issue was modelling and simulation tasks. Non-Random Two Liquids (NRTL) has been the most extended thermodynamic model used to fit the VLE experimental data due to the easy and accurate fitting of the required parameters^{27,41,49}. However, binary interaction parameters were not transferable from binary to ternary or more complex systems when ILs are presented, limiting their use in a process simulator as advised in a recent effort on modelling the complete phase equilibria for this separation and two IL solvents with CPA EoS⁵⁰. Therefore, only approximate methods based on the hydrocarbon *K*-values, taking them

independent from composition, have been developed and used in the literature^{19-22,35-37}. From this perspective and regarding recovery and regeneration section, merely flash distillation drums were able to be considered, due to their simplicity by contrast to distillation columns, which would have been simulated in a very simplified manner. Consequently, the benchmark approach reported in literature is a series of flashes³⁵. Thus, two flash distillation drums are destined for selectively recovering the extracted aliphatics at mild temperatures and vacuum conditions, whereas a final drum aims to separate the purified aromatics from the IL. Although this process configuration allows commercial purity for the aromatics, i.e. 99.9 wt.%, the recycling streams imply high vacuum operating conditions, high oversizing ratio in the extractor as well as high solvent consumption and, thus, determining the feasibility of the process³⁵. Other approaches from Jongmans et al. propose two flash distillation units, distillation columns and extraction units with supercritical CO₂; however, the core equipment is an extractive distillation column in that research, which implies achieving a standard purity in the bottom stream⁵¹. The same can be applied to the work by Kulajanpeng et al. regarding the regeneration steps after an extractive distillation column^{52,53}.

Leaving aside experimental-based approaches, *a priori* methods based on molecular simulation, such as COSMO-RS, has contributed in the development of the whole process as well as separation trains related to the aliphatic/aromatic separation and predicting vapor-liquid equilibria data involving aromatics and ILs^{34,38}. In this context, the methodology that combines COSMO-based thermodynamics predictions and Aspen Plus process simulators has been successfully applied in the past to solve this and other problematics⁵⁴⁻⁵⁶. An advantage of this proposed predictive methodology is the possibility to evaluate different process alternatives, as those reported in the literature, namely a flash distillation unit, a series of flash distillation units, and a stripper with N₂³⁴. As conclusion, a stripping column with N₂ fails attempting to achieve commercial standards for the aromatics but decreases operating costs, whereas a series of flashes enhance aromatic purities at the end of the process but increasing costs well above.

After reviewing the state-of-art of the matter, the development of an efficient separation process for simultaneously regenerating the IL and recovering the hydrocarbons needs to consider the next key facts:

- (i) IL maximum operating temperature (MOT) imposes a temperature limit in the IL regeneration process, frequently ranging 130 - 200 °C.
- (ii) Aliphatic/aromatic relative volatility increases as temperature decreases.

- (iii) Vacuum conditions or gas stripping means high aromatic recoveries/loses in the vapor.
- (iv) Selective ILs impose easier aromatic purification and regeneration processes.
- (v) A minimum of three equilibrium stages are needed to solve the separation train, whereas the higher the number of steps, the lower the aromatic loses.

The analysis of these facts reveals the next two basic design criteria:

- (i) Mild temperatures, higher number of steps and atmospheric pressure as enhancer conditions to separate selectively aliphatics and aromatics and to mitigate aromatic loses in the vapor and, thus, recycling streams and perturbations in the extractor.
- (ii) Temperature below MOT and vacuum or gas stripping to separate the aromatics and the IL. Vacuum and stripping agents stand as the two unique options to carry out the separation, safely working without IL thermal decomposition. Since vacuum is expensive, gas stripping stands as the leading proposal.

Stripping columns can simultaneously accomplish the two design criteria appended above. Firstly, a stripping column operating at atmospheric pressure, in absence of any stripping agent, may be a commitment point between mild temperatures and a reasonable number of stages to purify the aromatics and increase their recovery in comparison with previous proposals. The energy required can be distributed between the feed and the reboiler to make the column more effective. Secondly, once the aromatics have been purified, a second stripping column can be designed to separate the aromatics from the solvent. This second column can take advance of the residue temperature from the first column and use a stripping agent to ease the separation and avoid vacuum. After chilling the stream, a last flash distillation drum would separate the aromatics from the stripping agent, which can be recycled in the process avoiding conditioning. There are experimental evidences that support the technical feasibility of the different proposals evaluated in this group, dealing with distillation or stripping columns at pilot plant scale. In fact, Meindersma et al.¹⁶ reported that ILs' extractive properties were not modified in several extraction and regeneration cycles in a long-term experience at pilot plant. In addition to this, Larriba et al.³¹ also reported that ILs' extractive and physical properties were not altered after 5 consecutive extraction and regeneration cycles, being the regeneration step by distillation at 90 °C and 2 kPa for less than 1 hour. On the other hand, recent studies have demonstrated the reliability of COSMO-based/Aspen approach to describe separation by distillation of mixtures involving ionic liquids^{34,54-58}.

This work is focused on analyzing the suitability of this process configuration for IL regeneration stage by means of COSMO-based/Aspen Plus process simulations. In addition, the role of the IL nature in the separation process was evaluated by including a wide sample (100) of ILs from the ILUAM database, free available for Aspen Plus users⁵⁷. Firstly, a systematic screening was performed in the first stripping column to examine the effect of IL extractive properties on the recovery of both aromatic and aliphatic products. Afterwards, selecting a reduced number of representative ILs, the effect of operating conditions, namely temperature feed, column pressure, reboiler duty, and number of stages, on the aromatic/aliphatic separation in the stripping column were examined, considering different compositions of extract stream fed to first stripping column. From these outputs, this stripping column was designed to achieve aromatic purity specifications, comparing the results with those provided by a series of three flash distillation units, in terms of aromatic recovery, energy duty and operating cost. Finally, the two stripping columns were designed to completely demonstrate the feasibility of working in absence of vacuum but also improving current standards. This work contributes enhancing the technology for the purification and regeneration units when developing IL-based processes in which the IL should be regenerated by distillation.

2. Computational Details

2.1. COSMO-based/Aspen Plus Methodology

ILUAM database was directly used in this work to incorporate IL compounds in Aspen Plus process simulator, finding the details of the ILs available elsewhere⁵⁷. COSMOSAC, code 1, was selected as model specification to calculate activity coefficients since this approach mitigates the deviation when validating the methodology against the reliable experimental data involving aliphatics, aromatics and ILs, reported in recent works^{25,34}.

A binary mixture of hydrocarbons (*n*-heptane + toluene) was selected as model in this work, as widely done with excellent representativeness as can be found elsewhere²⁸. Extract streams were generated by simulating an extractor to separate toluene and *n*-heptane from a hydrocarbon mixture with a toluene mass fraction of 66.1 % and a solvent to feed (S/F) ratio of 5 in mass basis using different kind of ILs. This operation was simulated using the model EXTRACT at 313 K and 101.3 kPa with 10 equilibrium stages. All conditions were previously reported in previous works^{25,26}. The toluene content emulates the pyrolysis gasoline composition, which lastly entails the most used reference for the aromatic/aliphatic separation. In any case, the aromatic content in the source is not governing purity assessments

in the recovery process as can be found evaluating different aromatic sources with aromatic content ranging from 10 wt.% and 66 wt.%^{21,22}.

2.2. Conceptual Design of the Recovery and Regeneration Unit: Benchmark Process and Stripping Column-based Proposals

A simplified flow diagram of the benchmark processes reported in the literature is shown in Figure 1 (Process 1)³⁵. As remarked in the introduction section, the two first flash distillation units are intended to selectively remove *n*-heptane (FD1 and FD2), whereas the last flash distillation unit is used to carry out the toluene/IL separation (FD3).

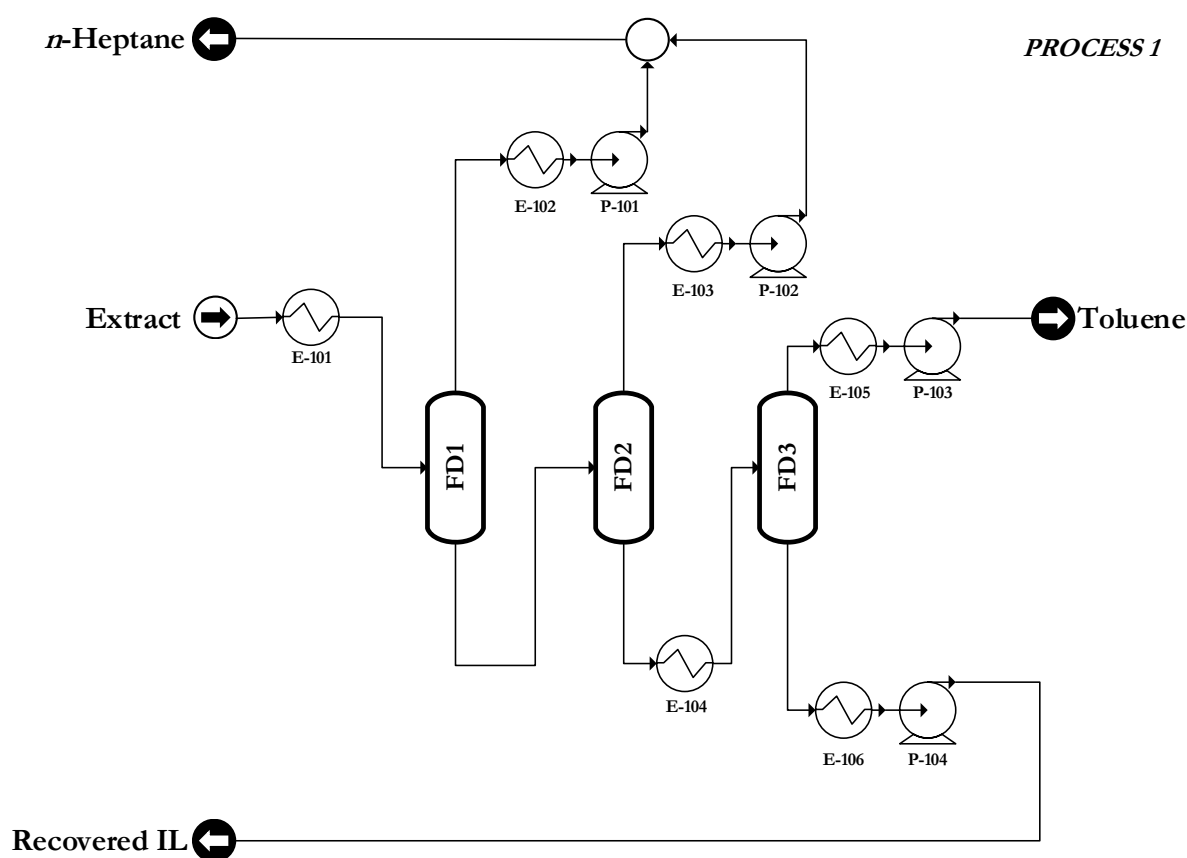


Figure 1. Benchmark Separation Train Process (Process 1) for IL Regeneration. Ref. 35.

The two stripping column-based processes examined in this work are depicted in Figure 2. The first approach includes a stripping column and a flash distillation unit (Process 2A), in order to compare the first stripping column with the two flash distillation units alternative in terms of aromatic recovery and operating costs. On the other hand, the main proposal (Process 2B) is integrated by two stripping columns. In both configurations, the first stripping column (SC1) selectively remove *n*-heptane in the vapor, recovering the toluene together with the IL in the residue stream. Afterwards, a flash distillation drum (FD3 in Process 2A) or second

stripping column (SC2 in Process 2B) separates the toluene from the IL solvent. A second stripping column (SC2 in Process 2B) requires an additional flash distillation unit (FD4) to separate toluene from the stripping gas (N_2).

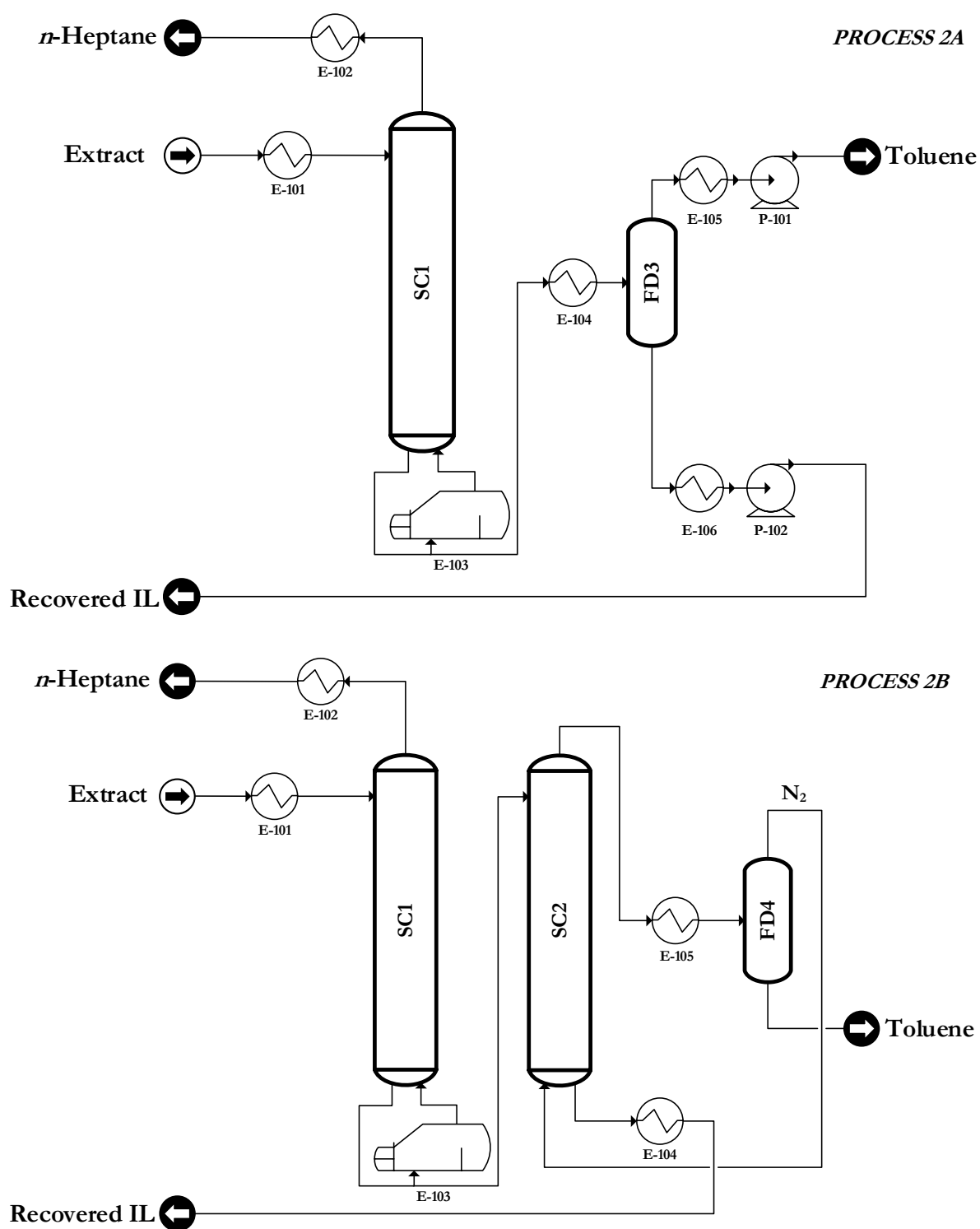


Figure 2. Proposed Separation Train Processes (Processes 2A and 2B) for IL Regeneration.

Flash distillation units were modelled by FLASH2. Heat exchangers were modeled by HEATER models, meanwhile PUMP model was destined to evaluated operations of pressure increase. In addition, vacuum consumption in each flash distillation unit was calculated by a compressor (COMPRESSOR model) emulating the same pressure drop directly to the vapor. To ease the comprehension, compressors destined to estimate vacuum are not detailed in the diagrams. Finally, stripping columns were simulated using RADFRAC models, running in equilibrium mode.

2.3. IL Screening in the Stripping Column

An IL screening was performed fixing an extract stream type 1, with the composition depicted in Table 1. Four extract stream types were selected covering two high capacity and two selective ILs to evaluate the conclusions in wide composition ranges. The extract stream is fed in the column at 90 °C, whereas the stripping column operates at 100 kPa and is initially designed with three equilibrium stages, feeding in the top stage and with heat flows in the reboiler (E-103) of 2200 and 5000 cal·s⁻¹. Two reboiler duties were initially adjusted and selected since it is expectable that each IL will required a different reboiler duty due to the different solvent-hydrocarbons interactions.

Table 1. Feed Compositions (*w*) and Flows (*m*) in the SC1

Compound	Extract type			
	1	2	3	4
w_{IL}	0.847	0.845	0.965	0.971
$w_{Toluene}$	0.120	0.118	0.034	0.028
$w_{n-Heptane}$	0.034	0.036	0.002	0.001
$m/ kg \cdot h^{-1}$	590.574	548.830	537.820	531.260

2.4. Sensitivity Analysis in the Stripping Column

A sensitivity analysis was performed for four representative ILs. Extract type compositions from 1 to 4 (Table 1), heat flow in the reboiler, number of stages, column pressure and feed temperature were independently examined. Toluene and *n*-heptane recoveries were tracked in liquid and vapor streams, respectively, for the sensitivity analysis steps. The balance of the required heat involving reboiler duty, feed temperature and vacuum, together with the number of stages in the column are the two main analysis to perform in the stripping column aiming at providing a compensate energy distribution together with an efficient number of equilibrium stages. For that purpose, first the number of stages is studied and fixed for the rest of the evaluations, which are expected to follow the same trend.

2.5. Process Simulation

Processes 1, 2A and 2B were simulated with the specifications depicted in Table 2. In Processes 2A and 2B, heat flow in the reboiler of SC1 adjusted the *n*-heptane recovery specifications, whereas in Process 1 the pressure of FD1 and FD2 are destined to accomplish the design specification, which were partial *n*-heptane recoveries of 60 % in FD1 and 90 % in FD2 based on literature [35]. The specification design target is set to a global 96 % recovery, imposing as design conditions in all cases. The separation of toluene from the IL is performed in Processes 1 and 2A at the MOT of the IL and at 3 kPa, whereas the feed conditions in SC2 in Process 2B are the residue temperature from SC1 and 100 kPa. Regarding the MOT set in Processes 1 and 2A, this value assays that the IL is thermally stable in the process based on TGA experiments. In addition to this, COSMO properly describes the non-volatile character of the IL at MOT and 3 kPa, not finding solvent losses in the vapor stream. To complete 2B scheme, FD4 properly separates toluene and the IL, feeding at 25 °C.

Table 2. Design Specifications of the Processes Simulated in this Work

Process	<i>n</i> -Heptane recovery	Feed conditions T (°C) / p (kPa)					
		SC1	FD1	FD2	FD3	SC2	FD4
1	96 % (vapor FD1 + FD2)		60/100	60/p	MOT/3		
2A	96 % (vapor SC1)	90/100	-	-	MOT/3		
2B	96 % (vapor SC1)	90/100	-	-	-	T/100	25/100

FD: Flash distillation and SC: Stripping column (Please see Figures 1 and 2 for details)

2.6. Estimation of Utilities and Operating Costs

Operating costs were estimated through the simplified flow diagrams depicted in Figures 1 and 2. Heating and cooling utilities were estimated by a proper utility selection from Aspen Plus database, whereas electricity was estimated by evaluating the pumps power. In any case, Aspen Economics permits to evaluate operating cost as a whole. To evaluate vacuum, the opposite pressure drop was emulated in Aspen Plus for the vapor stream using a compressor for that regard. The prices of the different vapor types, cooling water and electricity were directly used from Aspen Economics as detailed in Table 3.

Table 3. Costs^a of the Utilities Used from Aspen Economics

Utilities	Cost (\$·kJ)
Cooling water	$2.12 \cdot 10^{-7}$
Low pressure steam	$1.90 \cdot 10^{-6}$
Medium pressure steam	$2.20 \cdot 10^{-6}$
High pressure steam	$2.50 \cdot 10^{-6}$
Electricity	$1.58 \cdot 10^{-5}$

^a Extracted from Aspen Plus v10

3. Results and Discussion

3.1. Screening ILs in the Stripping Column to Separate Toluene from *n*-Heptane

The stripping column (SC1 in Figure 2) was simulated by COSMO-based/Aspen Plus to evaluate the role of IL nature on aromatic-aliphatic separation from extract stream, using composition 1 of Table 1). A wide sample of 100 ILs was included in the process simulation analysis using free ILUAM database⁵⁷. The recoveries (*R*) of toluene in the residue and *n*-heptane in the distillate of stripping column were used as parameters of separation efficiency:

$$R(\%) = \frac{100 \cdot m_{i,j}}{m_{i,feed}} \quad (1)$$

where *i* denotes the compound (toluene or *n*-heptane) and *j* refers to the stream (distillate or residue). Feed indicates the stream that is fed to the separation equipment. Figure 3 shows a cross plot of toluene recovery in the residue and *n*-heptane recovery in the distillate. Two different reboiler heats were used in these simulations, 2200 and 5000 cal·s⁻¹. The data is organized by IL families, establishing the anion and also the cation type (imidazolium, pyridinium and non-aromatic cations. As can be seen in Figure 3, *n*-heptane is mainly recovered by distillate stream whereas toluene is separated by residue. A wide range of hydrocarbon recoveries (closely from 0 to 100 %) was obtained depending on IL structure, which may be related to the different aromatic/aliphatic selectivities determined by the aromatic/aliphatic-IL intermolecular interactions⁵⁸.

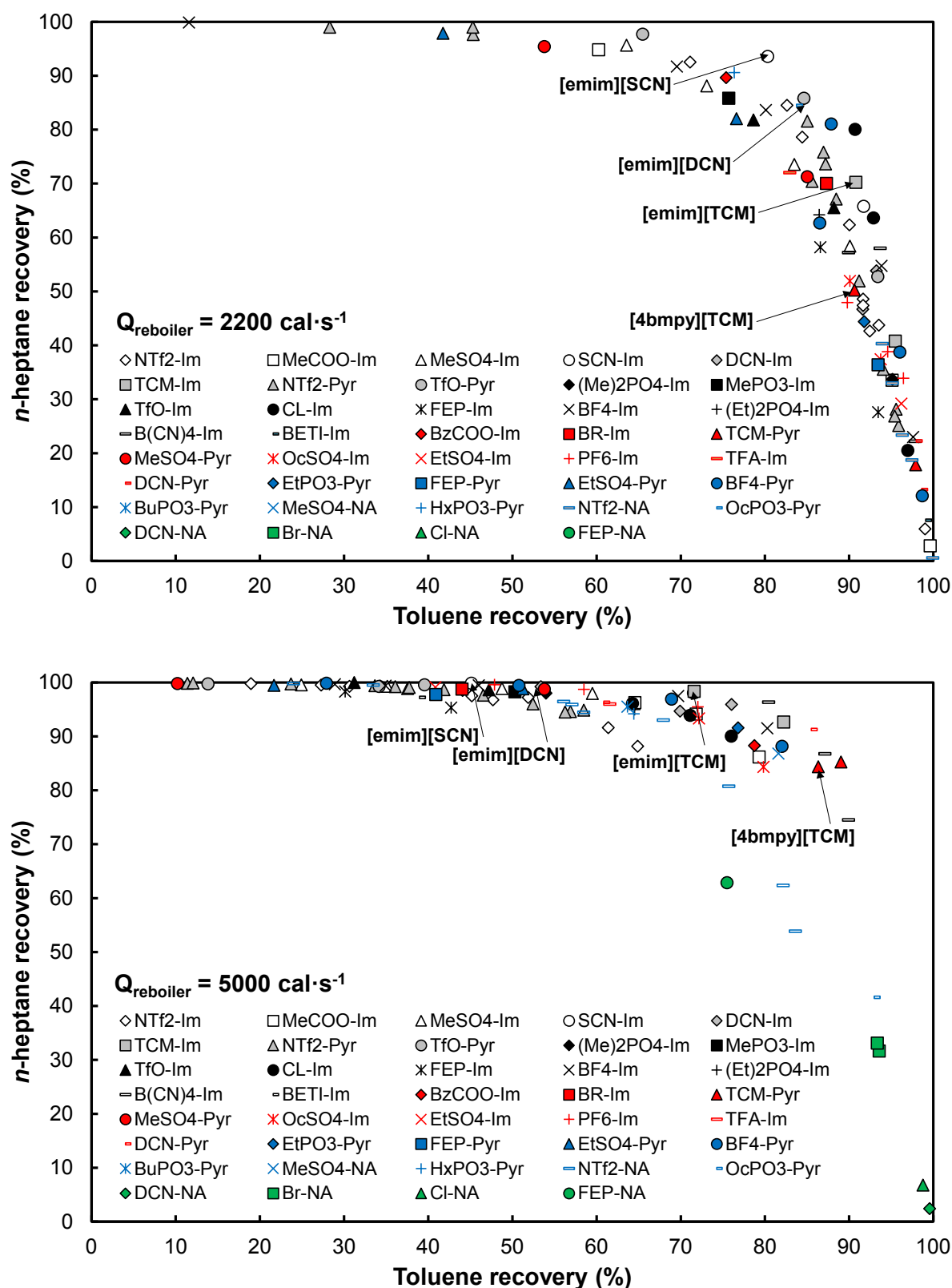


Figure 3. Toluene Recovery in the Residue and *n*-Heptane Recovery in the Distillate of Stripping Column 1 (SC1 in Figure 2) Organized by IL Families for Two Reboiler Duties.

As expected, the separation results are considerably dependent on the reboiler duty. In any case, the IL nature acts independently from reboiler duty. At $2200 \text{ cal}\cdot\text{s}^{-1}$, almost all the ILs

show high toluene recoveries in the liquid with relatively low *n*-heptane recoveries in the vapor. By contrast, at $5000 \text{ cal}\cdot\text{s}^{-1}$, aliphatic recoveries are significantly high for most of IL species due to the higher fraction of vaporized mixture in the bottom on the column, which also involves the aromatic component. From results in Figure 3, four ILs ([emim][SCN], [emim][DCN], [emim][TCM] and [4bmpy][TCM]) were selected for their representative entrainer behavior in the stripping column as well as their suitability to separate aromatics and aliphatics. Cyano-based ILs show considerably lower viscosities and higher thermal stability when compared to other ILs but also stand as the best candidates when evaluating their extractive properties^{18,23,59}. Their aromatic/aliphatic selectivity follows the trend [emim][SCN] > [emim][DCN] > [emim][TCM] > [4bmpy][TCM]; since aromatic/aliphatic selectivity inversely correlates with aromatic distribution ratios, higher selectivity implies higher recovery of *n*-heptane in distillate but lower recovery of toluene in the liquid residue⁶⁰.

To complement the analysis, the temperature achieved at the bottom of the stripping column (SC1) is depicted in Figure 4, displaying the temperature range from each representative IL family detailed above. As can be seen, a wide range of operating temperatures (100-175 °C) is also obtained. However, the obtained temperature in the reboiler is not an inconvenient since the MOT for suitable ILs in aromatic/aliphatic separation ranges from 139 to 207 °C^{31,59}.

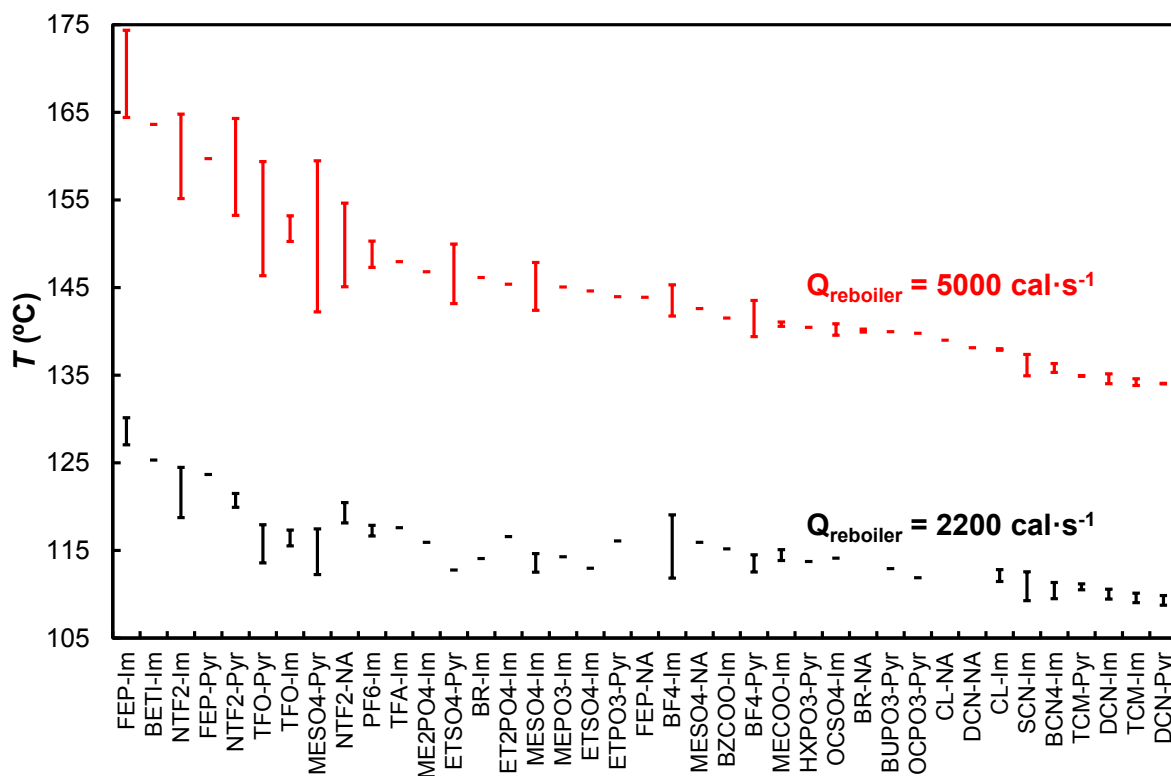


Figure 4. Temperatures in the Reboiler of the Stripping Column 1 (SC1) Organized by IL Families.

Current process simulation results suggest that the temperature in the reboiler would be below the thermal decomposition of the majority of the ILs, thus allowing the stability of the solvent. Moreover, reboiler temperature is a function of IL heat capacity and the aromatic recovery in the liquid, which imposed that selective ILs with low specific heats would be the best candidates; in this respect, cyano-based ILs stand again as the most adequate species from this new perspective.

In an effort to extend current analysis to a more general scenario, simulations of stripping column (SC1 with $Q_{\text{reboiler}} = 8000 \text{ cal}\cdot\text{s}^{-1}$) were carried out feeding the extract streams with different compositions collected in Table 1. Figure 5 shows that toluene and *n*-heptane recoveries follows different trends. A decrease in the *n*-heptane content in the extract stream (compositions from 1 to 4 in Table 1) clearly decreases its recovery on the vapor, whereas decreasing toluene content imposes a clear enhancement on its recovery in the liquid. The nature of the IL also plays a main role in the separation of the different extract streams by the stripping operation, remarking that ILs based on [SCN] and [DCN] anions presents a particular balanced behavior at low hydrocarbon content, with relatively high recovery (>80% for composition 4) of both toluene and *n*-heptane.

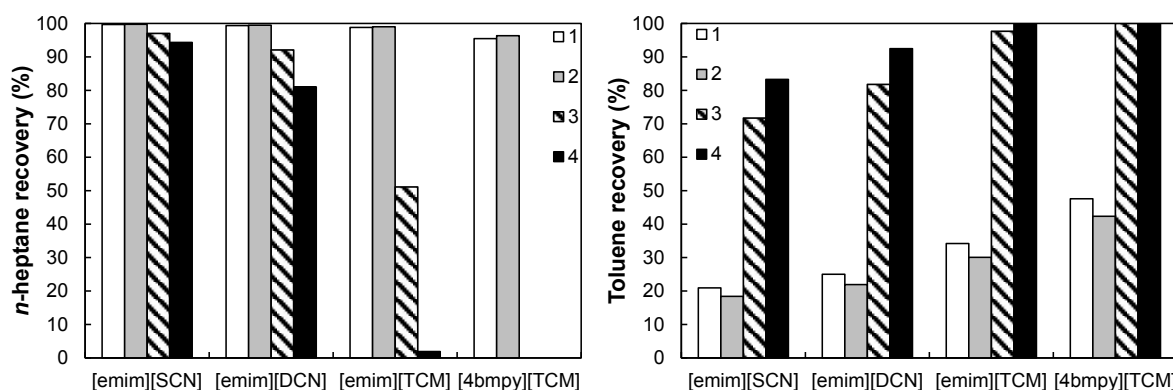


Figure 5. Hydrocarbon Recoveries for Different Extract Stream-type Compositions in Stripping Column 1 (SC1) Using $Q_{\text{reboiler}} = 8000 \text{ cal}\cdot\text{s}^{-1}$. The Series Are the Extract Streams, Detailed in Table 1.

3.2. Sensitivity analysis in SC1

The main operating variables of the SC1 column were analyzed, namely number of stages, reboiler duty, feed temperature and pressure, using the composition 1 of extract stream. Results are displayed in Figures 6 to 9. Figure 6 shows the effect of the number of equilibrium stages in the stripping column. As evidenced, the number of stages slightly improves the separation up to 4 stages when its impact remains negligible. Therefore, this number of stages is fixed in the next sensitivity analysis.

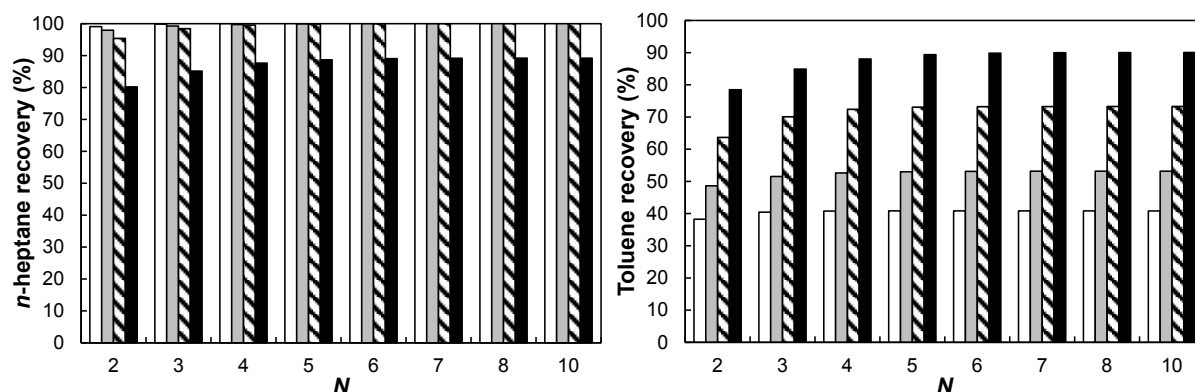


Figure 6. Sensitivity Analysis of Number of Stages (N) as a Function of n -Heptane and Toluene Recovery for SC1 in Processes 2A and 2B. Feed Temperature of 90 °C, Operating Pressure of 1 bar and Reboiler Duty of 5000 cal·s⁻¹. ILs: [emim][SCN], White; [emim][DCA], Grey; [emim][TCM], Grated; [4bmpy][TCM], Black.

Figure 7 collects the evolution of the hydrocarbon recoveries as function of the reboiler duty for the four selected IL considered. As expected, n -heptane recovery increases and toluene recovery decreases as the reboiler duty increases. Thus, a commitment election in these variables seems to be necessary to specify the stripping column. A clear IL effect is also observed in the separation results: the ILs with higher aromatic/aliphatic selectivity (those based on [DCN] and [SCN] anions) generally present higher hydrocarbon recoveries independently from the reboiler duty. Contrary, using ILs with lower selectivities (those base on [TCM] anion), the results are mainly affected by the reboiler duty, significantly increasing the recovery of n -heptane for higher reboiler heats.

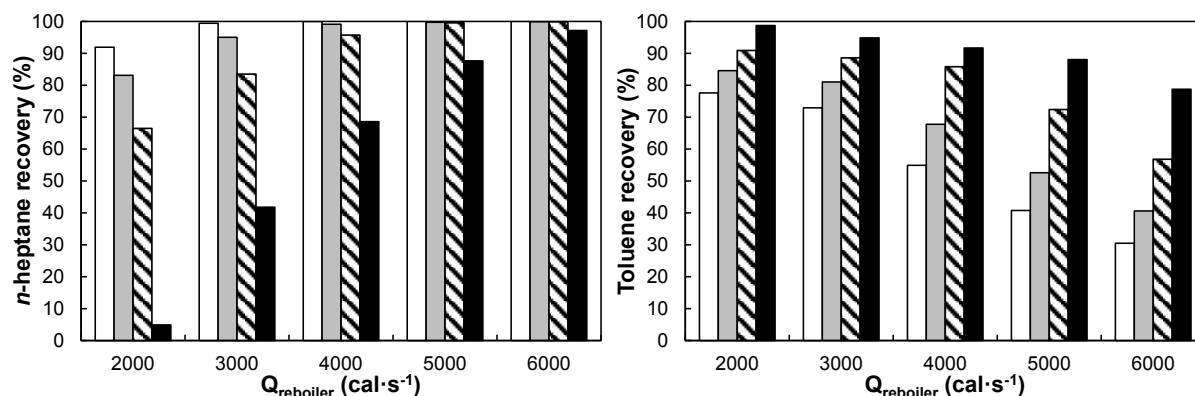


Figure 7. Sensitivity Analysis of Reboiler Duty (Q_{reboiler}) as a Function of n -Heptane and Toluene Recovery for SC1 in Processes 2A and 2B. Feed Temperature of 90 °C, Operating Pressure of 1 bar and 4 Equilibrium Stages. ILs: [emim][SCN], White; [emim][DCN], Grey; [emim][TCM], Grated; [4bmpy][TCM], Black.

Figure 8 presents the hydrocarbon recoveries obtained at different feed temperatures. Interestingly, close trends were obtained compared to those when changing the reboiler duty for the four selected ILs. n -Heptane recovery is almost the same in both scenarios, while toluene recovery is slightly more affected when modifying the feed temperature. This can be

related to a toluene vaporization at the top of the column, losing a great amount of toluene at temperatures over toluene boiling point (110.6 °C).

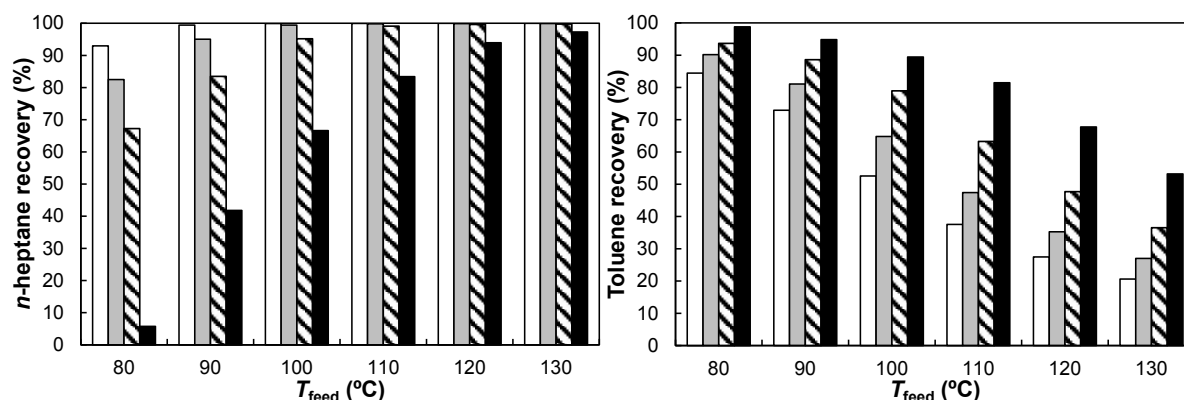


Figure 8. Sensitivity Analysis of Feed Temperature (T_{feed}) as a Function of n -Heptane and Toluene Recovery for SC1 in Processes 2A and 2B. Reboiler Duty of 5000 cal·s⁻¹, Operating Pressure of 1 bar and 4 Equilibrium Stages. ILs: [emim][SCN], White; [emim][DCN], Grey; [emim][TCM], Grated; [4bmpy][TCM], Black.

Figure 9 represents the evolution of the hydrocarbon recoveries as function of operating pressure for the four selected ILs. An expected trend is observed, the opposite effect than the heating the column. Nonetheless, vacuum enhances aliphatic recoveries but clearly deteriorates aromatic recoveries at very low pressures when comparing with heating approaches.

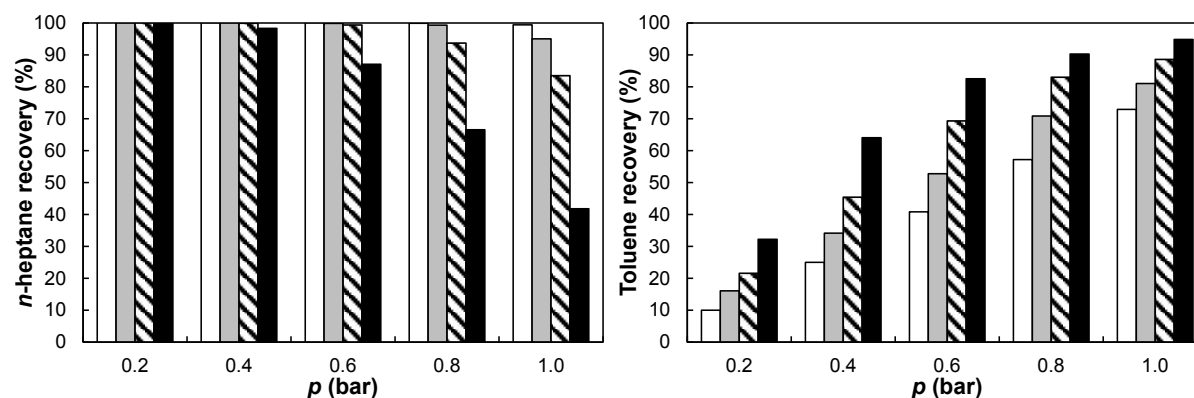


Figure 9. Sensitivity Analysis for Operating Pressure (p) for SC1 in Processes 2A and 2B. Reboiler Duty of 5000 cal·s⁻¹, Feed Temperature of 90 °C and 4 Equilibrium Stages. ILs: [emim][SCN], White; [emim][DCA], Grey; [emim][TCM], Grated; [4bmpy][TCM], Black

Overall, Table 4 collects the selected operating conditions for each IL in SC1, aiming at comparing Processes 2A and 2B with the benchmark Process 1.

357 **Table 4. Specified Operating Conditions for SC1 After Sensitivity Analysis**

IL	[emim][SCN]	[emim][DCN]	[emim][TCM]	[4bmpy][TCM]
N		4		
p / kPa		100		
T_{feed} / °C		90		
Q_{reboiler} / cal·s ⁻¹	2500	3200	4100	5800

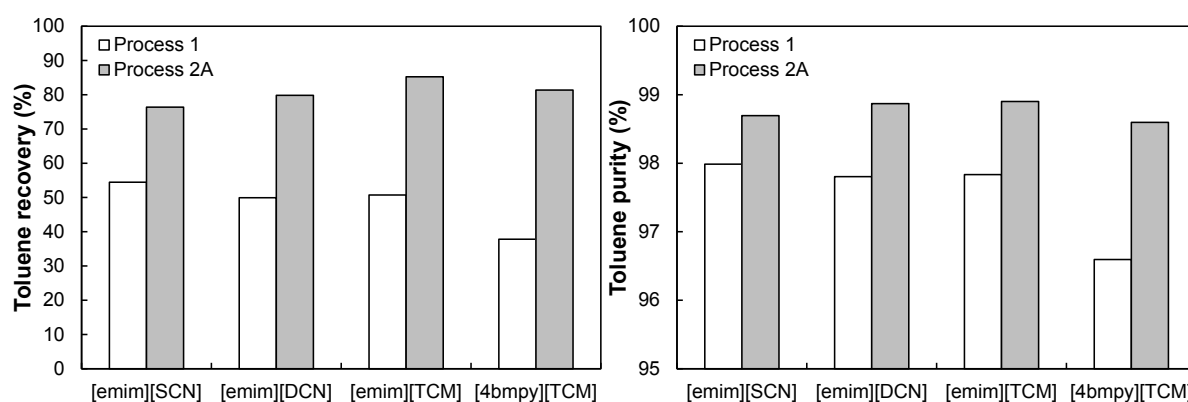
3.3. Comparison of SC1 and the Two flash Distillation Units to Separate the Hydrocarbons

Once stripping column main features have been analyzed, Processes 1 and 2A shall be compared in terms of aromatic recovery and operating costs, fixing aliphatic recovery. Firstly, conventional process (1) is compared with the first approach based on stripping columns (2A), showing the results in Figure 10. The pressure in FD1 and FD2 for Process 1 together with the MOT of the ILs are appended in Table 5.

Table 5. Specified Operating Conditions for Process 1 to Accomplish Design Specifications at Solvent Stability

IL	[emim][SCN]	[emim][DCN]	[emim][TCM]	[4bmpy][TCM]
p (FD1)/ kPa	43	33	28	16
p (FD2)/ kPa	17	13	11	6
MOT/ °C	87	139	179	174

As evidenced in Figure 10, the change of two distillation flashes by a stripping column implies almost doubling aromatic recovery with a significant decrease in the specific operating costs (per kg of aromatic recovery), mainly for those ILs with lower aromatic/aliphatic selectivities. It is also noteworthy that the new separation train also enhances aromatic purity.



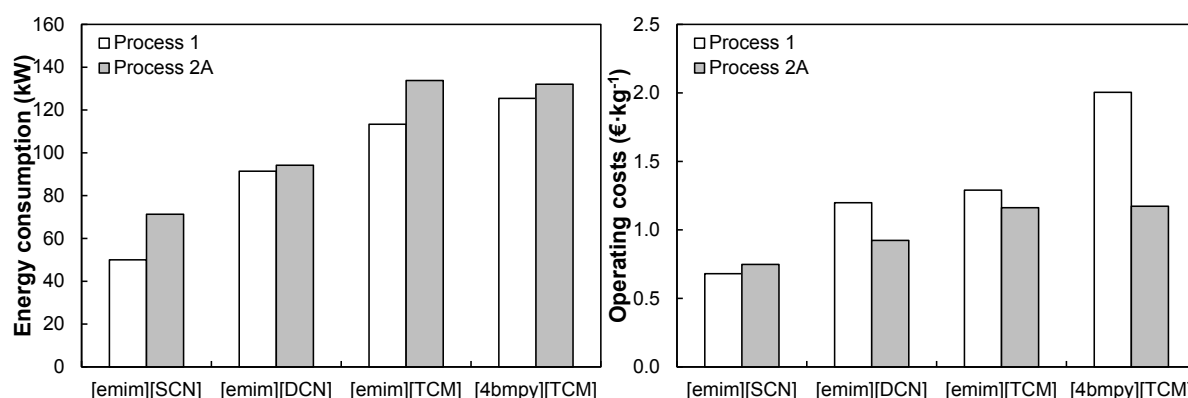


Figure 10. Separation Performance and Operating Insights for Processes 1 and 2A.

3.4. Stripping Columns Series to Avoid Vacuum Conditions

Finally, aiming at avoiding vacuum conditions in the whole process as a new paradigm to design liquid-liquid extraction processes with ILs, the operating costs of Process 2B were evaluated against Processes 1 and 2A. The separation performance of processes 2A and 2B regarding the hydrocarbons are coincident since SC1 is designed with the same specifications; hence, only operating costs are evaluated, specifying the same aromatic recovery in both cases (Figure 11). Although the cost analysis was performed considering only operating costs, fixed costs between the evaluated approaches are expected not to be governing cost differences. As evidenced, all ILs provide lower operating costs when avoiding vacuum conditions by using stripping columns (Process 2B) when comparing to flash distillation units (Process 2A). Even the role of the IL is less important for Process 2B, revealing also that two stripping columns means an improvement regardless the IL. The IL nature plays a crucial role in the separation, i.e. [emim][SCN] shows a more favorable VLE than the others that is less sensible to different process configuration, but a suitable design may bring closer solvent performances.

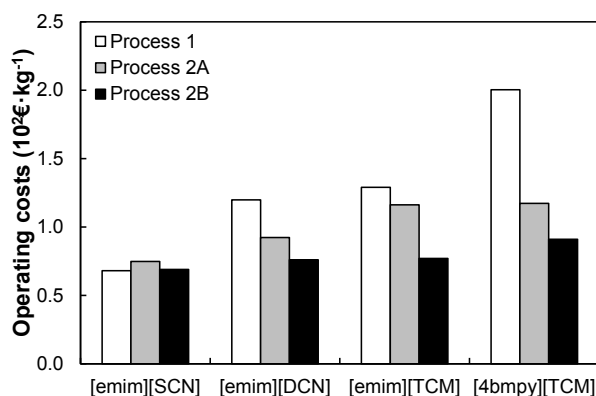


Figure 11. Operating Costs for Processes 1, 2A and 2B.

Conclusions

IL regeneration from extract streams in aromatic-aliphatic separation process by liquid-liquid extraction still constitutes a challenge to drive technology developments. In this work, a new separation train based on stripping columns was proposed and evaluated through COSMO-based/Aspen Plus computational methodology. Firstly, a systematic screening of ILUAM database accounting 100 ILs has highlighted the leading roles of the reboiler duty and the IL nature on aromatic and aliphatic recoveries. Secondly, after selecting feasible and representative ILs, the impact of stripping column operating conditions has been analyzed in details, namely reboiler duty, feed temperature, operating pressure and number of stages. *Ad hoc* reboiler duties to each solvent as well as feeding at 90 °C, working at atmospheric pressure, and 4 equilibrium stages are recommended. Thirdly, two approaches based on stripping columns, partially or totally avoiding vacuum, were compared with a three flash distillation series, which stands as the most promising approach reported in the literature. The role of the first stripping column, when compared with two flash distillation units, relies on enhanced separation effectiveness (almost twice) and lower specific operating cost. On the other hand, the use of a stripping column and a flash unit instead of an unique flash unit has proved to be preferably to design a stripping agent close-cycle (N₂) instead of dramatically decreasing the pressure to regenerate the IL and obtain the aromatic product. This new paradigm in the regeneration of ILs, here exemplified to the aromatic/aliphatic separation, can contribute in the development of more competitive IL-based processes in which non-volatile compounds can be separated from other compounds by distillation.

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.

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