Energy Fuels 32.4 (2018): 5650-5658

DOI: http://doi.org/10.1021/acs.energyfuels.8b00529

Novel Process to Reduce Benzene, Thiophene, and Pyrrole in Gasoline based on [4bmpy][TCM] Ionic Liquid

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Abstract

Regulations on benzene, nitro- and sulfur-containing aromatic hydrocarbon content in commercial gasolines are becoming more restrictive due to environmental and health issues. The benzene content in reformulated commercial gasoline is currently around 1 %. The reduction of benzene levels to comply with future regulations will imply significant changes in refinery configurations. This paper reports a novel extraction process to simultaneously separate benzene, thiophene, and pyrrole from a gasoline using the 1-butyl-4-metylpyridinium tricyanomethanide ([4bmpy][TCM]) ionic liquid (IL). A distillation sequence is also proposed for the isolation of the three aromatic hydrocarbons. The conceptual design of the whole process has been based on experimental data from the liquid-liquid extraction and vapor-liquid separation of benzene, thiophene, and pyrrole from isooctane using the IL [4bmpy][TCM]. A COSMO-based/Aspen Plus methodology has been used to simulate the conceptual design. The *a priori* COSMO-based/Aspen Plus approach was validated by comparison with the experimental liquid-liquid extraction results and conventional simulations based on experimental distribution ratios and *K*-values. Benzene, thiophene, and pyrrole contents in the gasoline would be reduced from 5.0 % to 0.1 % using the proposed process with a solvent-to-feed mass ratio of 5.0 and also three streams with high content in each aromatic would be obtained. Increasing the solvent-to-feed mass ratio above 5.0, benzene content in the treated gasoline could be reduced up to 200 ppm.

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1. INTRODUCTION

Benzene has been identified as the major contributor to cancer risk among the hydrocarbons forming commercial gasoline.[1] In addition, the presence of nitrogen- and sulfur-containing hydrocarbons in gasoline implies NO_x and SO_x emissions that cause acid rain and respiratory problems.[2,3] For these reasons, regulations such as the Rule for Control of Emissions of Hazardous Air Pollutants from Mobile Sources in US or the Directive 2009/30/CE in the European Union have recently reduced the maximum content of benzene in automotive fuels below 1 %.[4,5] Moreover, more restrictive regulations on the benzene and sulfur-containing hydrocarbons contents in gasoline are expected in the near future.[6] Current designs of refineries are not capable to assay these incoming purity standards. A wide refinery redesign would be needed to reduce the benzene content under 0.6 vol. % and also a reformulation of blended gasolines due to the reduction in the octane number.[1] Because of this, we have developed the conceptual design of a novel extraction process based on ILs to reduce the benzene, thiophene, and pyrrole contents in gasolines and thus to comply with more restrictive regulations without modifying refinery configurations.

ILs have been proposed as potential replacements of conventional organic solvents due to their nonvolatile nature, wide liquid range, and tunable properties.[7] Specifically, ILs have been extensively studied in the extraction of benzene, toluene, ethylbenzene, and xylenes (BTEX) from *n*-alkanes.[8-12] In addition, a wide number of papers have been focused on the extraction of nitrogen- and sulfur-containing aromatic hydrocarbons using ILs.[2,13-23] However, the great majority of works has studied simplified binary mixtures such as the extraction of toluene or thiophene from *n*-alkanes[24-27] and the recovery of the extracted hydrocarbons from the IL has been hardly investigated.[28]

In this work, the [4bmpy][TCM] IL has been selected as solvent for the simultaneous extraction of benzene, thiophene, and pyrrole from isooctane due to its high thermal stability, low viscosity, and high recyclability, but first and foremost due to its high capacity to extract aromatics.[29] The vapor-liquid recovery of the extracted aromatics from the IL-based solvent have been also done. From the experimental hydrocarbon distribution ratios, we have simulated the extractor using the Kremser method. On the other hand, the experimental *K*-values obtained in the vapor-liquid separation of the hydrocarbons from the IL have been used to apply the algorithm developed by Navarro et *al*. to simulate flash distillation units with high IL concentration.[28] Kremser method has been used to select the optimal temperature in the extractor and the Navarro et *al*. algorithm was used to find suitable temperature and pressure combinations in the flash distillation units that form the recovery section. Both methods require experimental data and, therefore, they are only suitable to simulate separation processes within the experimental boundaries. Hence, the above methodology is not capable to deal with a more realistic gasoline model compose of a large number of hydrocarbons, which would be no possible to experimentally manage. To simulate the separation process for a gasoline model formed by 14 hydrocarbons, we have selected an *a priori* approach, the COSMO-based/Aspen Plus methodology.[30] This recently developed methodology has been revealed as a powerful tool to be used in the conceptual design of new separation processes for multicomponent mixtures based on ILs without the need of having experimental data.[30] To date, COSMO-based/Aspen Plus methodology has been applied in the design of alternative process using ILs for aromatic extraction,[31] CO_2 absorption,[32] toluene absorption,[33] and absorption refrigeration cycles.[34,35]

The validation of the *a priori* COSMO-based/Aspen Plus approach has been made first by comparing the predictions with the experimental liquid-liquid equilibrium data of the ternary

systems (benzene, thiophene or pyrrole + isooctane + [4bmpy][TCM]). Isooctane was selected as reference in the ternary systems to represent the non-aromatic content in gasolines. This compound is used as reference standard in the octane number scale with a Research Octane Number of 100.[36] In addition, a comparative analysis between the results obtained using the experimental data-based simulations of the extractor by the Kremser method and flash distillation simulations by the Navarro et *al*. algorithm[28] with those using the COSMO-based/Aspen Plus methodology was also performed for a simplified stream formed by isooctane, benzene, thiophene, and pyrrole.

Once the COSMO-based/Aspen Plus approach was validated, the optimization and simulation of the proposed process was done for a more realistic gasoline formed by 14 hydrocarbons with the composition listed in Table 1. This stream was formed by a 10 wt. % of toluene, *p*-xylene, 1,2,4-trimethylbenzene, and C_6-C_8 isoalkane hydrocarbons because their octane numbers are higher or equal to 100.[36] *p*-Xylene has been chosen as benchmark for C_8 aromatic hydrocarbons and 1,2,4-trimethylbenzene for the C_9-C_{10} aromatic hydrocarbons in the gasoline model. Toluene, *p*-xylene, and 1,2,4-trimethylbenzene contents in the gasoline model are based on the usual composition of commercial gasolines.[37] In addition, a 5 wt. % of benzene, pyrrole, thiophene, C_6-C_8 *n*-alkanes, and C_6-C_7 cycloalkanes was fixed to evaluate the performance of the IL in the extraction of benzene, pyrrole, and thiophene from *n*-alkanes, cycloalkanes, isoalkanes, and other aromatic hydrocarbons with a similar boiling range.

In Figure 1, the flow diagram of the proposed process to extract benzene, thiophene, and pyrrole from the gasoline is depicted. The first section of the process is formed by a liquid-liquid extraction column (T-100) where the untreated gasoline and the [4bmpy][TCM] are fed in a countercurrent flow. A raffinate stream, the treated gasoline, is withdrawn from the top of the extractor. The extract, the IL loaded with the aromatic hydrocarbons, exits the bottom of

the extractor. The second section is formed by three flash distillation units (V-100, V-101, and V-102) to selectively recover the extracted hydrocarbons from the IL. The IL [4bmpy][TCM] was revealed as an efficient mass agent in the vapor-liquid separation of aliphatic and aromatic hydrocarbons in our previous work, substantially increasing the aliphatic/aromatic relative volatility.[29] For that reason, the V-100 and V-101 flash distillation units were destined to selectively recover and recycling of the extracted non-aromatic hydrocarbons from the IL. The rich non-aromatic streams from the top of V-100 and V-101 are recycled to the bottom of the extractor. The bottoms stream from V-101, substantially free of non-aromatic impurities, is sent to the V-102 flash distillation unit where the aromatic product is separated from the IL. Lean IL from the bottom of V-102 is returned to the extractor. The aromatic product is recovered overhead and sent to the third section formed by three conventional distillation columns. A benzene-rich stream is recovered from the first column (T-101), a thiophene-rich stream from the second column (T-102), and a pyrrole-rich stream from the third column (T-103). Finally, the toluene-rich stream is mixed with the treated gasoline stream to increase the octane number of the gasoline product.

2. EXPERIMENTAL SECTION

2.1. Chemicals. [4bmpy][TCM] was acquired from Iolitec GmbH with a mass fraction purity higher than 0.98, a water content of 129 ppm and a halide content lower than 0.5 %. Handling of the IL was made inside a glove box filled with dry nitrogen to avoid hydration. The structure of [4bmpy][TCM] is shown in Figure 2. Benzene, pyrrole, thiophene were purchased from Sigma-Aldrich, whereas isooctane was supplied by Merck with the purities listed in Table 2.

2.2. Experimental liquid-liquid extraction procedure. Liquid-liquid equilibrium experiments of benzene, thiophene, or pyrrole from isooctane using [4bmpy][TCM] was made in 8 mL glass vials over the whole range of composition of the ternary systems at 313.2 K. Raffinate phases were analyzed in an Agilent 7890A gas chromatograph equipped with a liquid autosampler Agilent 7693, whereas the extract phases were analyzed by Headspace Gas Chromatography (HS-GC) in the Agilent 7890A gas chromatograph using an Agilent 7697A headspace sampler. The complete description of the analytical method used to determine the composition of raffinate and extract phases can be found elsewhere.[38]

In addition to the above ternary liquid-liquid equilibrium experiments, the simultaneous extraction of benzene, thiophene, and pyrrole from a mixture with isooctane containing 1000 ppm of each aromatic hydrocarbon was performed using [4bmpy][TCM] at 303.2, 313.2, and 323.2 K and solvent-to-feed ratios (S/F) in mass of 1.0, 2.0, 3.0, 4.0, and 5.0. Raffinate and extract phases obtained in these experiments were analyzed as described above for the ternary liquid-liquid equilibrium experiments.

2.3. Simulation of the liquid-liquid extractor by the Kremser Method. From the results obtained in the simultaneous extraction of benzene, thiophene, and pyrrole from isooctane, a countercurrent liquid-liquid extractor was simulated using the Kremser method, analogous to the method used in absorption. The parameters used in the Kremser method were the extraction factor (E) and the reciprocal of E (U) calculated from the experimental values of distribution ratios (D_i) for each hydrocarbon:

$$E_i = D_i \frac{V}{L} \tag{1}$$

$$U_i = \frac{1}{E_i} = \frac{L}{D_i V} \tag{2}$$

where D_i is the experimental distribution ratio, L denotes the raffinate mass flow, and V is the extract mass flow. From the experimental distribution ratios of the hydrocarbons at 323.2 K and an S/F ratio in mass of 2.0, flows of raffinate and extract streams were estimated calculating total balances for each component. Using the experimental values of D_i and fixing a mass flow of 1000 t/h for the feed, the extractor was simulated using an iterative method implemented in Microsoft Excel. This method was employed in our previous works in the simulation of the dearomatization of pyrolysis and reformer gasolines using ILs.[23,39] The influence of the number of equilibrium stages (N_s) in the extractor on the yield of extraction of benzene, thiophene, and pyrrole was studied in the simulations. The results obtained in the simulations by the Kremser method were compared with those obtained by the COSMO-based/Aspen Plus methodology under the same conditions.

2.4. Experimental vapor-liquid separation of the extracted hydrocarbons from the IL. The extracted hydrocarbons are recovered from the IL using flash distillation units as a result of the nonvolatile nature of the IL and the aforementioned improvement of the aliphatic/aromatic relative volatility in the presence of IL. The vapor-liquid recovery of the extracted hydrocarbons from [4bmpy][TCM] was experimentally studied for the feed composition of each flash distillation unit. The required vapor-liquid equilibria data between benzene, thiophene, pyrrole, isooctane, and [4bmpy][TCM] were determined using the Agilent 7697A headspace sampler coupled to the Agilent GC 7890A at temperatures between 323.2 K and 423.2 K. These temperatures were selected considering the maximum operation temperature for [4bmpy][TCM] that ensures the thermal stability of the IL for 1 year (447 K).[29] The complete description of the HS-GC method to determine the vapor-liquid equilibria between hydrocarbons and ILs can be found in our previous publication.[40]

2.5. Simulation of the vapor-liquid separation of the extracted hydrocarbons. To simulate the flash distillation units, the experimental *K*-values for each hydrocarbon obtained by the HS-GC method were used. Adiabatic flash simulations was performed at different temperatures and pressures using the algorithm published by Navarro et *al*. for mixtures formed by ILs and hydrocarbons.[28] In addition, the three flash distillation units were simulated using the COSMO-based/Aspen Plus methodology at the same temperatures and pressures used in the Navarro et *al*. algorithm.

2.6. Simulation of the proposed process by the COSMO-based/Aspen Plus methodology. To define [4bmpy][TCM] in the database of Aspen Plus, the molecular geometry of the IL was optimized using TURBOMOLE with DFT method B88-P86 (bp) and TZVP basis set. In this case, the molecular model formed by independent anions (Cation + Anion) was employed in the geometry optimization. The IL was described in Aspen Plus V8.8 as pseudo-component introducing its density, molecular weight, molecular volume, σ-profile, and normal boiling temperature. These properties were obtained in the COSMOthermX program package (version C30_1201, BP_TZVP_C30_1201, default parametrization). The introduction of ILs in Aspen Plus using COSMO-based calculations has been extensively described in our previous publication.[30] In the simulation of the proposed process, a gasoline model formed by 14 hydrocarbons was employed with the composition previously listed in Table 1. All the hydrocarbons forming the gasoline were selected as conventional compounds from the Aspen Plus database.

The COSMOSAC property model was selected to calculate the activity coefficients in the simulations. Specifically, we have employed the modification to the Lin and Sandler model (mode 3 of COSMOSAC model) developed by Lin, Mathias et *al*. (2002) because this

COSMO-based equation exhibited the lowest values of mean absolute percentage error in the prediction of activity coefficients at infinite dilution of a wide variety of solutes in ILs.[30,41]

An adiabatic Aspen Plus EXTRACT rigorous model with 20 equilibrium stages at 323 K and 101.3 kPa was used to simulate the extractor (T-100). The IL was introduced in the stage 1 and the gasoline in the stage 20. The recycled streams obtained in the first and second flash distillation units (V-100) and (V-101) were introduced at 323 K and 101.3 kPa in the stages 18 and 19 of the extractor. The FLASH2 model was employed to simulate the three flash distillation units used to recover the extracted hydrocarbons from the IL.

To simulate the separation of the extracted hydrocarbons in the conventional distillation columns, the DSTWU model was selected. This model uses the Winn-Underwood-Gilliland method, fixing the recovery of heavy and light key components. Recoveries of light and heavy key components were selected to ensure the convergence of the simulations using 10 equilibrium stages in each distillation column. The first distillation column (T-101) operates at 101.3 kPa with a 99 % of benzene recovery (light key component) and a 0.5 % of thiophene recovery (heavy key component) in the distillate. In the second distillation column (T-102), thiophene was selected as light key component with a 99 % of recovery in the distillate whereas toluene was the heavy key component with a 1 % of recovery in the distillate; this column also operates at 101.3 kPa. Finally, the third distillation column has the aim of separating toluene from pyrrole at 60.8 kPa. For that purpose, toluene was fixed as the light key component with a 99.9 % of recovery in the distillate and the pyrrole recovery was fixed to 2.5 %. The toluene-rich stream obtained in the distillate was mixed with the raffinate from the extraction column to obtain the treated gasoline.

3. RESULTS AND DISCUSSION

3.1. Liquid-liquid extraction of benzene, thiophene, or pyrrole from isooctane using [4bmpy][TCM]. Experimental determination and COSMO-based/Aspen Plus predictions. The experimental liquid-liquid equilibria for the {isooctane + (benzene, thiophene, or pyrrole) + [4bmpy][TCM]} ternary systems at 313.2 K are plotted in Figure 3 and listed in Table S1 of the Supporting Information. As seen, the solubility of the aromatic hydrocarbons was considerably higher than that of isooctane in the IL. Specifically, the pyrrole was completely miscible with the IL, whereas the solubility of benzene in the IL was 0.792 and for the thiophene was 0.944 in mole basis. These high values of solubility confirm the high affinity of the IL-based solvent for the three aromatic hydrocarbons.

In Figure 3, predictions for the ternary liquid-liquid equilibria using the COSMO-based/Aspen Plus approach are plotted together with the experimental data. As can be seen, the predicted tie-lines were almost coincident with the experimental values at low content in the three aromatic hydrocarbons. This result is essential to perform the simulation of the proposed process of extraction of benzene, thiophene, and pyrrole from gasoline, since the content of the three aromatic hydrocarbons in the gasoline will be lower than 5 wt. %. The largest deviations of the predictions were observed for the extraction of benzene, being the experimental solubility slightly higher than that predicted by the COSMO-based/Aspen Plus approach. In the case of thiophene, the predicted solubility in the IL was slightly higher than the experimental value and COSMO-based calculations predicted a phenomenon of solutropy that does not exist in the experimental results. However, the predicted tie line slopes were very similar to the experimental at low values of thiophene. On the other hand, the experimental ternary liquid-liquid equilibria obtained in the extraction of the pyrrole was almost coincident with the predictions from the COSMO-based/Aspen Plus methodology. Considering the low deviations between experimental and predicted ternary liquid-liquid

equilibria at low contents of aromatic hydrocarbons, the COSMO-based/Aspen Plus predictions seems to be adequate to be used in the conceptual design of the extraction process of benzene, thiophene, and pyrrole from gasolines.

From the experimental results of the ternary liquid-liquid equilibria, the aromatic distribution ratios (D_{arom}) and aromatic/isooctane selectivities ($\alpha_{arom,isooctane}$) were calculated as follows:

$$D_{arom} = \frac{w_{aromatic}^{extract}}{w_{aromatic}^{raffinate}} \quad (3)$$

$$\alpha_{arom,isooctane} = \frac{D_{arom}}{D_{isooctane}} \quad (4)$$

where w_i are the experimental mass fractions of benzene, thiophene, or pyrrole in the raffinate and extract phases. Experimental values of D_{arom} and $\alpha_{arom,isooctane}$ are listed as a function of composition in Table S1 of the Supporting Information. For comparative purposes, the highest values of aromatic distribution ratios and aromatic/isooctane selectivities for the three ternary systems are listed in Table 3; these values were obtained at the lowest aromatic content in the feed. The pyrrole was extracted with very high values of mass-based distribution ratios and pyrrole/isooctane selectivities. These results are due to the similarity between the structure of the pyrrole and the pyridinium-based cation. The replacement of the nitrogen atom in the pyrrole by the sulfur in the thiophene has substantially decreased the values of the distribution ratio and the selectivity in the extraction from isooctane. In the case of benzene, both extractive properties were slightly smaller than those in the extraction of thiophene.

According to the results obtained, nitrogen-containing aromatic hydrocarbons will be more easily extracted from gasolines using the IL [4bmpy][TCM] than those containing sulfur or BTEX. These conclusions are in agreement with Hansmeier et *al*. (2011), who concluded that

nitrogen-containing aromatic hydrocarbons are better extracted than sulfur-containing aromatic hydrocarbons using ILs.[24]

3.2. Experimental simultaneous extraction of benzene, thiophene, and pyrrole from isooctane. The performance of [4bmpy][TCM] in the simultaneous extraction of the three aromatic hydrocarbons was studied for mixtures of isooctane with contents of 1000 ppm of every aromatic. This composition was selected to represent a low content of benzene, thiophene, and pyrrole in the extractor of the proposed process. From the experimental results, yield of extraction of isooctane and total yield of extraction of the aromatic hydrocarbons were calculated with the following expressions:

$$Yld_{\text{isooctane}}(\%) = 100\frac{m_{\text{isooctane}}^{\text{extract}}}{m_{\text{isooctane}}^{\text{feed}}} \tag{5}$$

$$Yld_{\text{arom}}(\%) = 100\frac{m_{\text{benzene}}^{\text{extract}} + m_{\text{thiophene}}^{\text{extract}} + m_{\text{pyrrole}}^{\text{extract}}}{m_{\text{benzene}}^{\text{feed}} + m_{\text{thiophene}}^{\text{feed}} + m_{\text{pyrrole}}^{\text{feed}}} \tag{6}$$

where m_i are the masses of each hydrocarbon added to the vial or determined in the extract phase. Experimental yields of extraction as a function of temperature and mass-based solvent-to-feed ratio are depicted in Figure 4. As observed, the yield of extraction of aromatic hydrocarbons was substantially higher than that for isooctane. This result is in agreement with the high value of aromatic/isooctane selectivities obtained in the ternary liquid-liquid equilibria. The effect of temperature on the yield of extraction of aromatic hydrocarbons was more significant than that observed for the isooctane. Therefore, a temperature of 323.2 K seems to be the optimal to separate these compounds and thus this temperature will be used in the simulation of the proposed process. On the other hand, the effect of S/F ratio on the yield of extraction of aromatic hydrocarbons was lower than that on the extraction of isooctane. For instance, The Yld_{arom} at 323.2 K using S/F ratios of 2.0 and 5.0 were 70.1 % and 79.8 %, respectively. On the other hand, the $Yld_{\text{isooctane}}$ increased from 3.2 to 7.3 % using S/F ratios of

2.0 and 5.0, respectively. Therefore, to minimize the co-extraction of isooctane and to reduce investment and operating costs, a S/F ratio of 2.0 was selected as the most adequate to perform the separation of benzene, thiophene, and pyrrole from isooctane.

3.3. Simulation of the extraction of benzene, thiophene, and pyrrole from isooctane using the Kremser method and the COSMO-based/Aspen Plus methodology. The liquid-liquid extraction of the three aromatic hydrocarbons from isooctane in a countercurrent extractor was also simulated using the Kremser method and the COSMO-based/Aspen Plus methodology. Simulations were performed at 323.2 K and a S/F ratio in mass of 2.0 as a function of number of equilibrium stages. The feed stream was the isooctane mixture with contents of 1000 ppm of benzene, thiophene, and pyrrole above-mentioned. The experimental distribution ratios of each hydrocarbon calculated from the experimental liquid-liquid equilibrium at 323.2 K and S/F ratio of 2.0 were used in the Kremser method.

Yields of extraction of benzene, thiophene, and pyrrole were calculated from the flows and compositions obtained in the simulations. In Figure 5, the results obtained by the Kremser method and the COSMO-based/Aspen Plus methodology are depicted. As seen, the results obtained for the pyrrole were almost coincident using both simulation methods, obtaining a yield of extraction almost complete at all number of stages employed because of the high solubility of pyrrole in [4bmpy][TCM]. In the case of thiophene, COSMO/Aspen Plus predicted slightly higher yields of extraction than the Kremser method at N_s between 2 and 8. This difference can be explained because the COSMO-based calculations slightly overestimated the experimental thiophene solubility in [4bmpy][TCM] as concluded in the analysis of the ternary liquid-liquid equilibria data for the system {isooctane + thiophene + [4bmpy][TCM]}. The largest deviations between both methods used in the simulations were obtained for the yields of extraction of benzene. COSMO-based simulations estimated lower

values of $Yld_{benzene}$ than the Kremser method over the whole range of the number of equilibrium stages in the extractor. These differences can be caused because the Kremser method assumes a constant benzene distribution ratio along the column, whereas the COSMO-based/Aspen Plus methodology calculates the liquid-liquid equilibrium in each stage. Analyzing the results obtained in the simulation of the extractor using both methods, the *a priori* COSMO-based/Aspen Plus approach provides results comparable to those obtained by the experimental data-based Kremser method. Because of this, the application of COSMO-based/Aspen Plus methodology to develop the conceptual design of the proposed process to extract benzene, thiophene, and pyrrole from gasoline seems to be adequate.

3.4. Simulation of the vapor-liquid separation of the extracted hydrocarbons. The simulation of the recovery section has been performed using the algorithm developed by Navarro et *al*. based in the experimental *K*-values of each hydrocarbon in the presence of ILs[28] and the COSMO-based/Aspen Plus methodology. To simulate the first flash distillation, experimental data of vapor-liquid equilibria between the extracted hydrocarbons and [4bmpy][TCM] with a mixture composition equal to that of the extract stream calculated from the simulation of the extractor at temperatures from 323 K to 373 K were obtained. Results from the experimental determination of the vapor-liquid equilibria are listed in Table S2 in the Supporting Information. The objective of the first flash distillation unit was to recover approximately the 50 % of the extracted isooctane. To obtain this recovery, the operating conditions of the first flash were fixed at 323 K and 10 kPa, since the highest values of isooctane/aromatic relative volatilities were obtained at the lowest temperature. The second flash distillation unit also operates at 323 K but the pressure was reduced at 3 kPa to volatilize the remaining isooctane in the IL. Finally, the aim of the third flash distillation unit was to recover the aromatic hydrocarbons from the IL. Because of this, experimental vapor-liquid

equilibria were also determined at 423 K. This temperature is substantially lower than the maximum operating temperature (447 K) for [4bmpy][TCM] that ensures the use of this IL for at least 1 year without thermal decomposition.[29] The pressure of the third flash distillation unit was fixed at 0.5 kPa to increase the aromatic hydrocarbon recovery from the IL.

From the mass flow and composition values of the feed and vapor streams obtained from the simulations of the flash distillation units, values of the recovery of isooctane ($R_{\text{isooctane}}$) and aromatics (R_{arom}) were calculated using the following equations:

$$R_{\text{isooctane}}(\%) = 100\frac{\left(m_{\text{isooctane}}\right)_{\text{vapor stream}}}{\left(m_{\text{isooctane}}\right)_{\text{feed}}} \tag{7}$$

$$R_{\text{arom}}(\%) = 100\frac{\left(m_{\text{benzene}} + m_{\text{thiophene}} + m_{\text{pyrrole}}\right)_{\text{vapor stream}}}{\left(m_{\text{benzene}} + m_{\text{thiophene}} + m_{\text{pyrrole}}\right)_{\text{feed}}} \tag{8}$$

In Table 4, a comparison between the values of $R_{\text{isooctane}}$ and R_{arom} obtained by the Navarro et *al*. algorithm and the COSMO-based/Aspen Plus approach for the three flash distillation units is reported. The recovery of the isooctane was substantially higher than the aromatic recovery for both simulation methods. Therefore, the COSMO-based/Aspen Plus methodology has successfully predicted the entrainer effect caused by the IL [4bmpy][TCM] that increases the isooctane/aromatic relative volatility. The effect of temperature and pressure in the flash distillations units on the hydrocarbon recovery was also correctly described by both simulation methods. Hence, these results confirm the applicability of the COSMO-based/Aspen Plus approach to simulate the whole extraction process of aromatic hydrocarbons from gasolines considering both extraction and recovery sections.

3.5. Simulation of the proposed process to extract benzene, thiophene, and pyrrole from gasoline using [4bmpy][TCM]. In the simulation of the whole process, we have used for the extractor the optimized temperature determined from the experimental liquid-liquid

equilibrium data (323.2 K) and the temperature and pressure optimized for each flash distillation units by the Navarro et *al*. algorithm (323.2 K and 10 kPa for V-100, 323.2 K and 3 kPa for V-101, and 423.2 K and 0.5 kPa for V-102). The main objective of the simulations was to determine the effect of S/F ratio on the benzene, thiophene, and pyrrole contents in the treated gasoline. For that reason, simulations were performed at S/F ratios from 0.5 to 9.0 obtaining the results shown in Figure 6. As a result of the high solubility of pyrrole in the IL, the percentage of this aromatic hydrocarbon in the treated gasoline is almost constant with the S/F ratio. In the case of thiophene, employing a solvent-to-feed ratio higher than 4.0 the content of this sulfur-containing aromatic hydrocarbon in the treated gasoline would be lower than 0.06 wt. %. Finally, the effect of S/F ratio on the benzene content in the treated gasoline was the most significant because this aromatic hydrocarbon is the less soluble in [4bmpy][TCM]. As observed, using a mass-based S/F ratio of 5.0, the benzene content in the treated gasoline would be reduced from 5.0 wt. % to 0.05 wt. %. In addition, a treated gasoline with 200 ppm of benzene could be obtained using a S/F ratio of 7.0. Therefore, this proposed process would be used to comply with highly restrictive regulations on benzene content in gasoline. The benzene content in the final treated gasoline was lower than those for thiophene and pyrrole at S/F ratios greater than 5.0 because the toluene rich-stream obtained in the third distillation column has small quantities of thiophene and pyrrole that increases the content of both aromatic hydrocarbons in the treated gasoline.

The aim of the three distillation columns of the proposed process is to obtain three by-product streams with high contents in benzene, thiophene, and pyrrole and to recover the extracted toluene to be mixed with the treated gasoline obtained from the liquid-liquid extraction column to increase its octane number. In Figure 6, purities of benzene, pyrrole, and thiophene in the by-product streams obtained in the distillation columns are also shown. The

bottom stream obtained from the third distillation column had a purity of pyrrole higher than 99.7 wt. % in all simulations because the boiling point of this nitrogen-containing aromatic hydrocarbon is different enough than that of the toluene. The purity of thiophene obtained from the second distillation column decreased at S/F higher than 2.5 because the co-extraction of other compounds, such as *n*-octane or cycloheptane. In the case of benzene, its purity in the distillate of the first distillation column increased at S/F values between 0.5 and 5.0 because the yield of extraction of this aromatic hydrocarbon also rose. By contrast, the benzene purity decreased at S/F ratios greater than 5.0 because of the co-extraction of isohexane, *n*-hexane, and cyclohexane. Analyzing the global results, a S/F ratio of 5.0 seems to be the optimal to obtain very low aromatic contents in the final gasoline and to obtain three by-product streams formed by benzene, thiophene, and pyrrole with purities that ensure their commercial value. However, this S/F ratio could be increased to reduce the benzene content in the treated gasoline up to 200 ppm. Flows, temperatures, pressures and compositions of the streams obtained in the simulation of the proposed process at a S/F ratio of 5.0 are listed in Table S3 in the Supporting Information.

To sum up, the proposed process of extraction of benzene, thiophene, and pyrrole from gasoline using [4bmpy][TCM] with a S/F ratio of 5.0 would reduce the content of these three aromatic hydrocarbons from 5.0 % to 0.1 % in the gasoline, obtaining also three valuable by-product streams with a 91.3 wt. % of benzene, 99.8 wt. % of pyrrole, and 92.3 wt. % of thiophene, respectively.

4. CONCLUSIONS

In this paper, the conceptual design of a novel process to reduce benzene, thiophene, and pyrrole content in gasoline based on the IL [4bmpy][TCM] has been developed using

experimental data and the *a priori* COSMO-based/Aspen Plus methodology. Firstly, the liquid-liquid equilibria for the ternary system (benzene, thiophene, or pyrrole + isooctane + [4bmpy][TCM]) were experimentally determined at 313.2 K. The ternary diagrams were adequately predicted by the COSMO-based/Aspen Plus methodology. High values of aromatic/isooctane selectivities and aromatic distribution ratios were obtained using [4bmpy][TCM]; therefore, this IL is adequate to be applied in the extraction of benzene, thiophene, and pyrrole from gasolines. The simultaneous extraction of the three aromatic hydrocarbons from isooctane and the recovery of the extracted hydrocarbons from the solvent were also experimentally studied. From the experimental data, the extractor and the recovery section formed by three flash distillation units were simulated using the Kremser method and the Navarro et *al*. algorithm, respectively. The results obtained in the experimental-based simulation methods were comparable to those employing the *a priori* COSMO-based/Aspen Plus approach. Because of this, the conceptual design of the process to reduce the benzene, thiophene, and pyrrole content in a gasoline formed by *n*-alkanes, isoalkanes, cycloalkanes, and aromatic hydrocarbons was made using the COSMO-based/Aspen Plus methodology. The complete process was simulated at several solvent-to-feed ratios to optimize this variable. Using a S/F ratio of 5.0, the benzene, thiophene, and pyrrole contents in the gasoline were reduced from 5.0 wt. % to 0.1 wt. %. In addition, three product streams with high contents in benzene, thiophene, and pyrrole could be obtained in a separation section formed by three distillation columns. Increasing the S/F ratio the benzene content in the treated gasoline could be reduced up to 200 ppm. Hence, the proposed process could be applied in the future to accomplish more restrictive regulations on benzene, nitrogen-containing, or sulphur-containing aromatic hydrocarbons without modifying the currently used structure of refineries.

ACKNOWLEDGMENT

The authors are grateful to Ministerio de Economía y Competitividad (MINECO) of Spain and Comunidad Autónoma de Madrid for financial support of Projects CTQ2014–53655-R and S2013/MAE-2800, respectively. N.D.M. thanks MINECO for her FPI grant (Reference BES–2015–072855) and M.L. also thanks MINECO for his Juan de la Cierva-Formación Contract (Reference FJCI-2015-25343). P.N. thanks Fundação para a Ciência e a Tecnologia for awarding him a postdoctoral grant (Reference SFRH/BPD/117084/2016).

Supporting Information.

Experimental liquid-liquid equilibrium and vapor-liquid equilibrium data and flows, temperatures, pressures, and compositions obtained in the simulation of the proposed process.

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Table 1. Composition of the Gasoline used in the COSMO-based/Aspen Plus Simulation of the Proposed Process for the Simultaneous Extraction of Benzene, Pyrrole, and Thiophene

Hydrocarbon	wt.%
Benzene	5.0
Pyrrole	5.0
Thiophene	5.0
n-Hexane	5.0
Isohexane	10.0
Cyclohexane	5.0
n-Heptane	5.0
Isoheptane	10.0
Cycloheptane	5.0
n-Octane	5.0
Isooctane	10.0
Toluene	10.0
p-Xylene	10.0
1,2,4-trimethylbenzene	10.0

Table 2. Specifications of the Chemicals

Chemical	Supplier	Mass Fraction Purity	Analysis Method
[4bmpy][TCM][a]	Iolitec GmbH	0.98	NMR[b] and IC[c]
Benzene	Sigma–Aldrich	0.998	GC[d]
Thiophene	Sigma–Aldrich	0.99	GC[d]
Pyrrole	Sigma–Aldrich	0.98	GC[d]
Isooctane	Merck	0.995	GC[d]

[a] [4bmpy][TCM] = 1-butyl-4-methylpyridinium tricyanomethanide
[b] Nuclear Magnetic Resonance
[c] Ion Chromatography
[d] Gas Chromatography

Table 3. Maximum Values of Mass-based Aromatic Distribution Ratio (D_{arom}) and Aromatic/isooctane Selectivity ($\alpha_{arom,isooctane}$) in the {isooctane + aromatic + [4bmpy][TCM]} Ternary Liquid-liquid Equilibria at 313.2 K

Aromatic Extracted	Maximum Mass-based D_{arom}	Maximum $\alpha_{arom,isooctane}$
Benzene	0.80	65.6
Thiophene	1.16	81.4
Pyrrole	48.1	4141.9

Table 4. Recovery of Isooctane and Aromatic Hydrocarbons from the [4bmpy][TCM] in the Three Flash Distillation Units Simulated by the Navarro et *al*. Algorithm[28] and by COSMO-based/Aspen Plus Methodology

Method	**V-100** (323.2 K, 10 kPa)		**V-101** (323.2 K, 3 kPa)		**V-102** (423.2 K, 0.5 kPa)	
Navarro et *al*. Algorithm	R_{isooct} / %	R_{arom} / %	R_{isooct} / %	R_{arom} / %	R_{isooct} / %	R_{arom} / %
	60.66	3.52	70.67	7.55	99.98	77.6
COSMO-based/ Aspen Plus	R_{isooct} / %	R_{arom} / %	R_{isooct} / %	R_{arom} / %	R_{isooct} / %	R_{arom} / %
	52.52	6.04	72.00	11.63	98.79	71.6

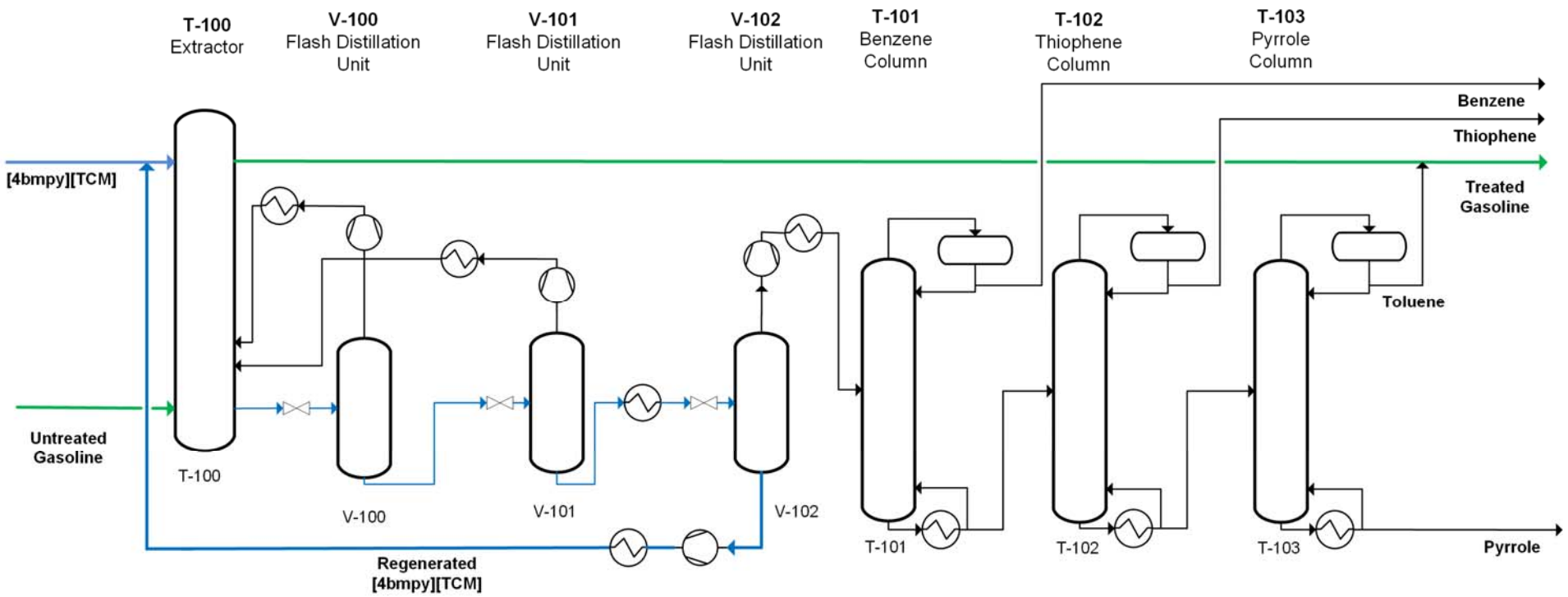


Figure 1. Flow diagram of the proposed process to reduce benzene, thiophene, and pyrrole content in gasoline using the ionic liquid [4bmpy][TCM] as solvent.

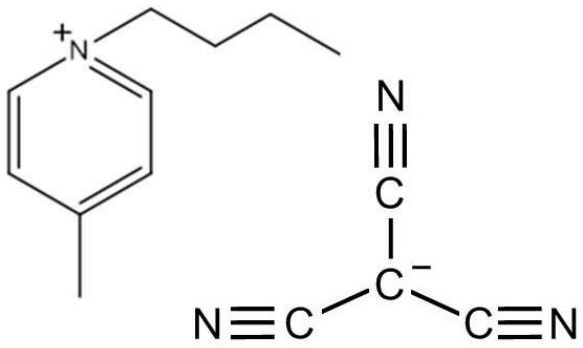
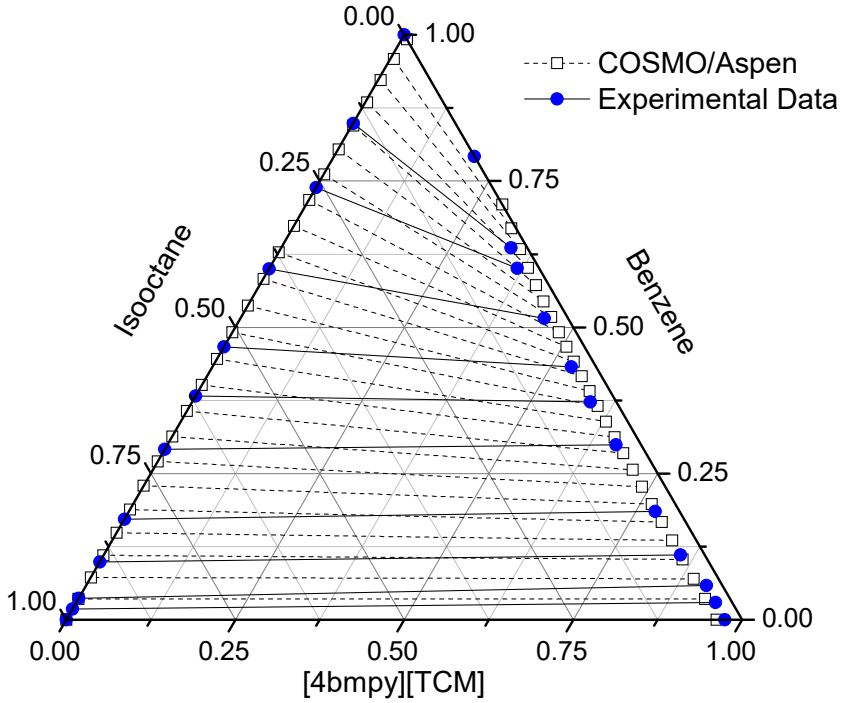


Figure 2. Structure of the 1-butyl-4-metylpyridinium tricyanomethanide ([4bmpy][TCM]) ionic liquid.


0.00
1.00
0.25
0.75
0.50
0.50
0.75
0.25
1.00
0.00
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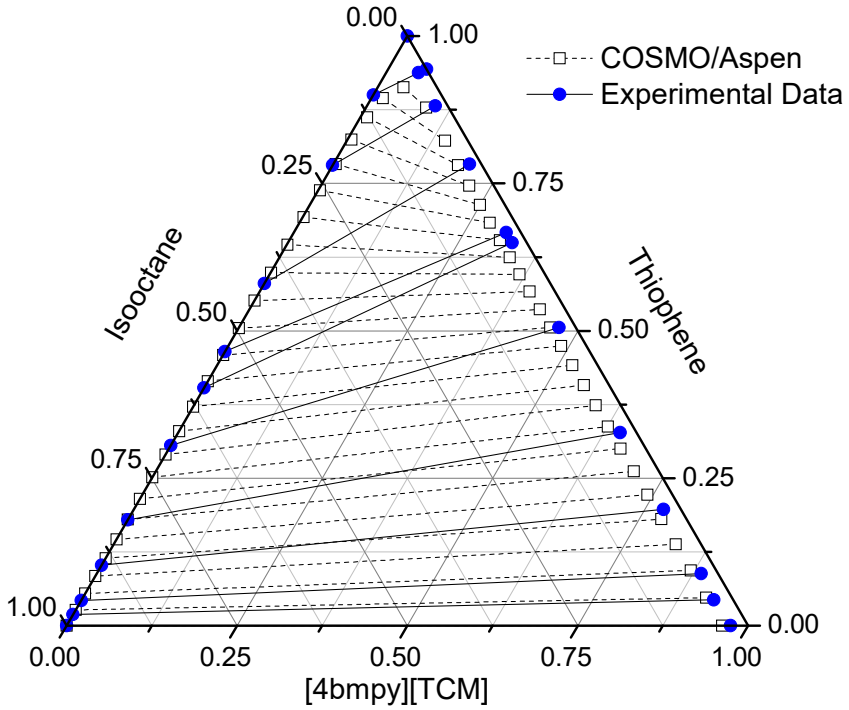
0.50
0.75
1.00
Isooctane
Benzene
[4bmpy][TCM]
COSMO/Aspen
Experimental Data


0.00
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0.75
1.00
Isooctane
Thiophene
[4bmpy][TCM]
COSMO/Aspen
Experimental Data

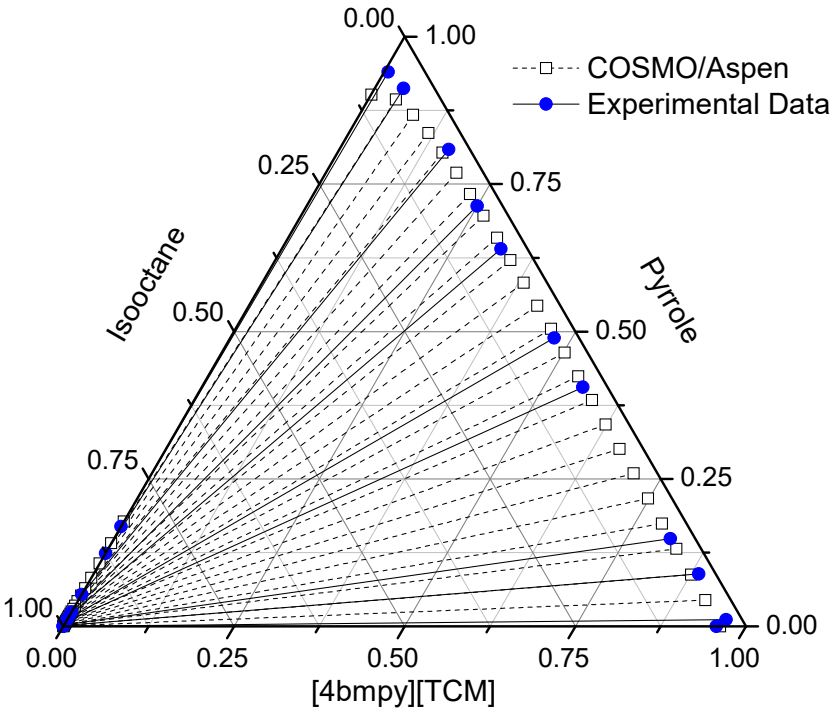

Figure 3. Ternary liquid-liquid equilibrium in the extraction of benzene, thiophene, and pyrrole from isooctane using [4bmpy][TCM] at 313.2 K. Solid lines and blue points are experimental tie-lines whereas dashed lines and empty squares are COSMO-based/Aspen Plus predictions.

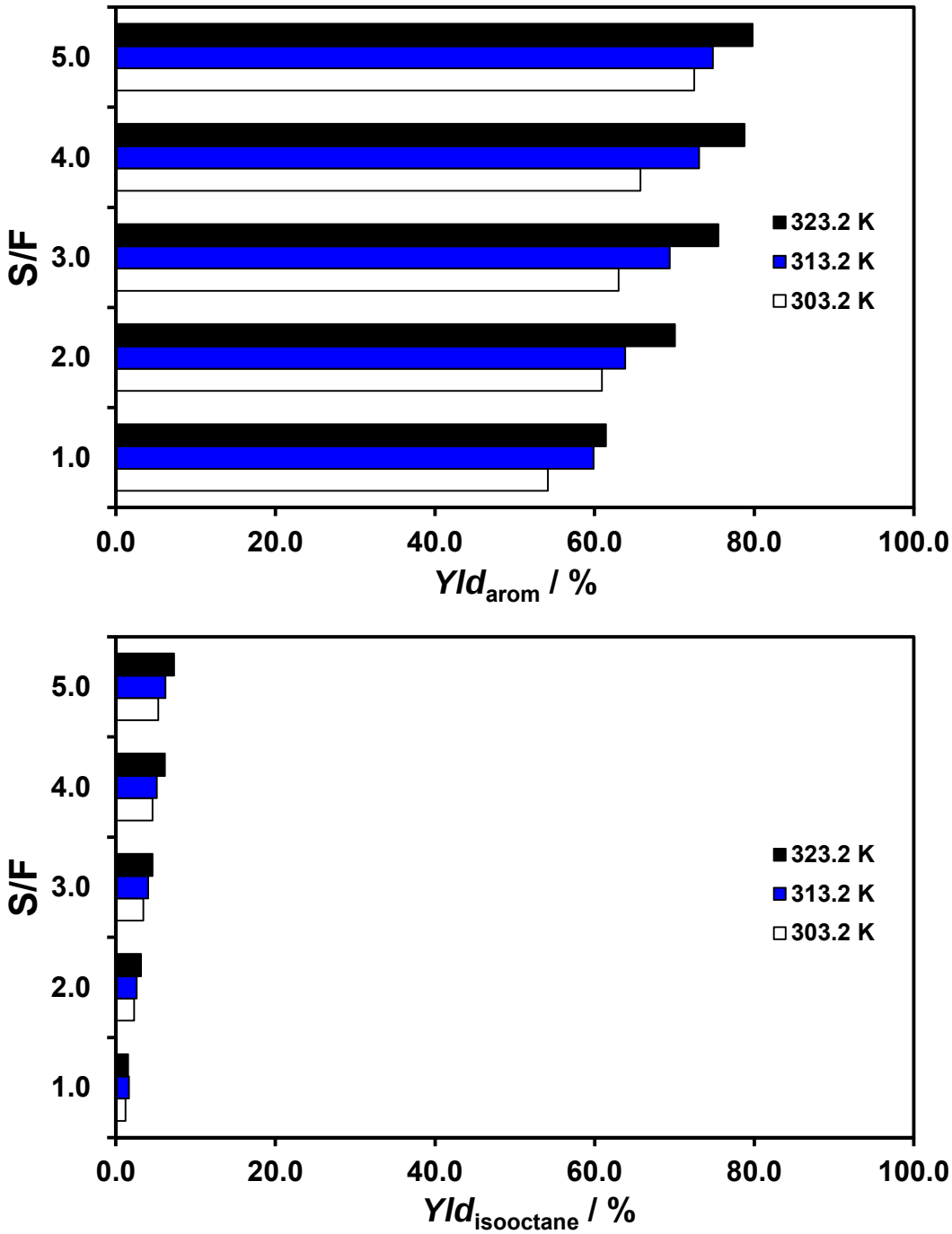

Figure 4. Yields of extraction of aromatic hydrocarbons and isooctane as a function of temperature and S/F ratio in the simultaneous extraction of benzene, thiophene, and pyrrole from a mixture with 1000 ppm of each aromatic hydrocarbon using [4bmpy][TCM].

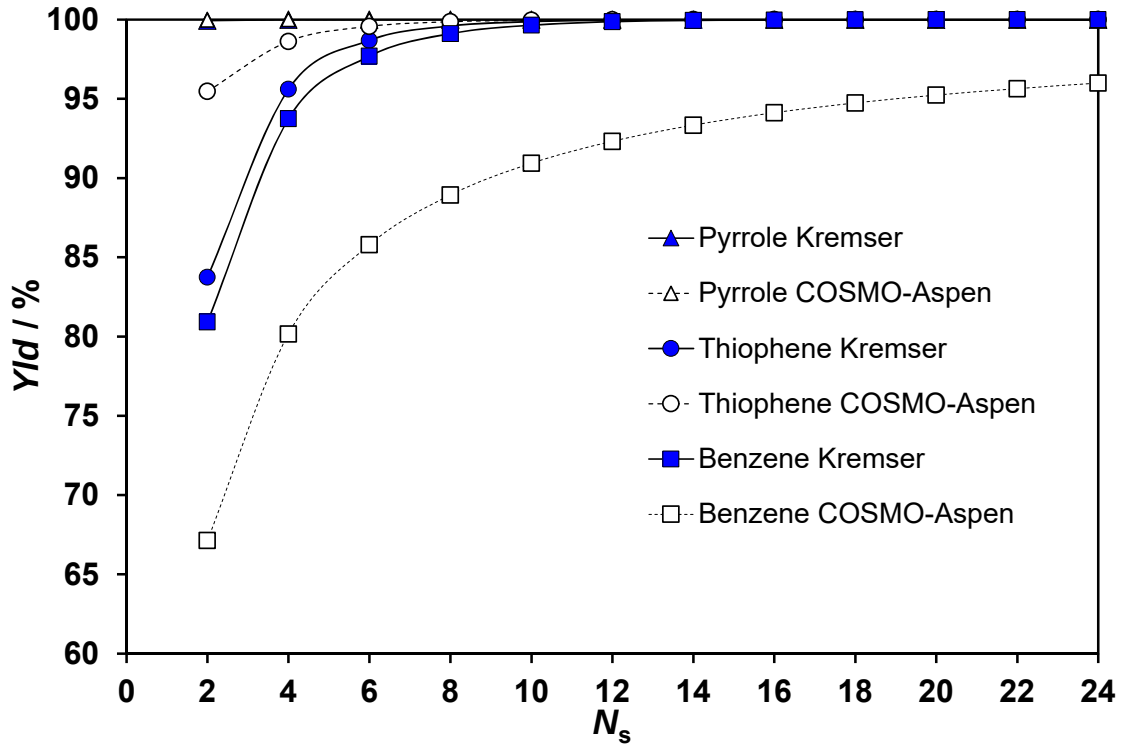

Figure 5. Yield of extraction of benzene, thiophene, and pyrrole from isooctane in the simulation of the extractor at 323.2 K and a S/F of 2.0 as a function of the number of equilibrium stages by the Kremser Method and the COSMO-based/Aspen Plus methodology.

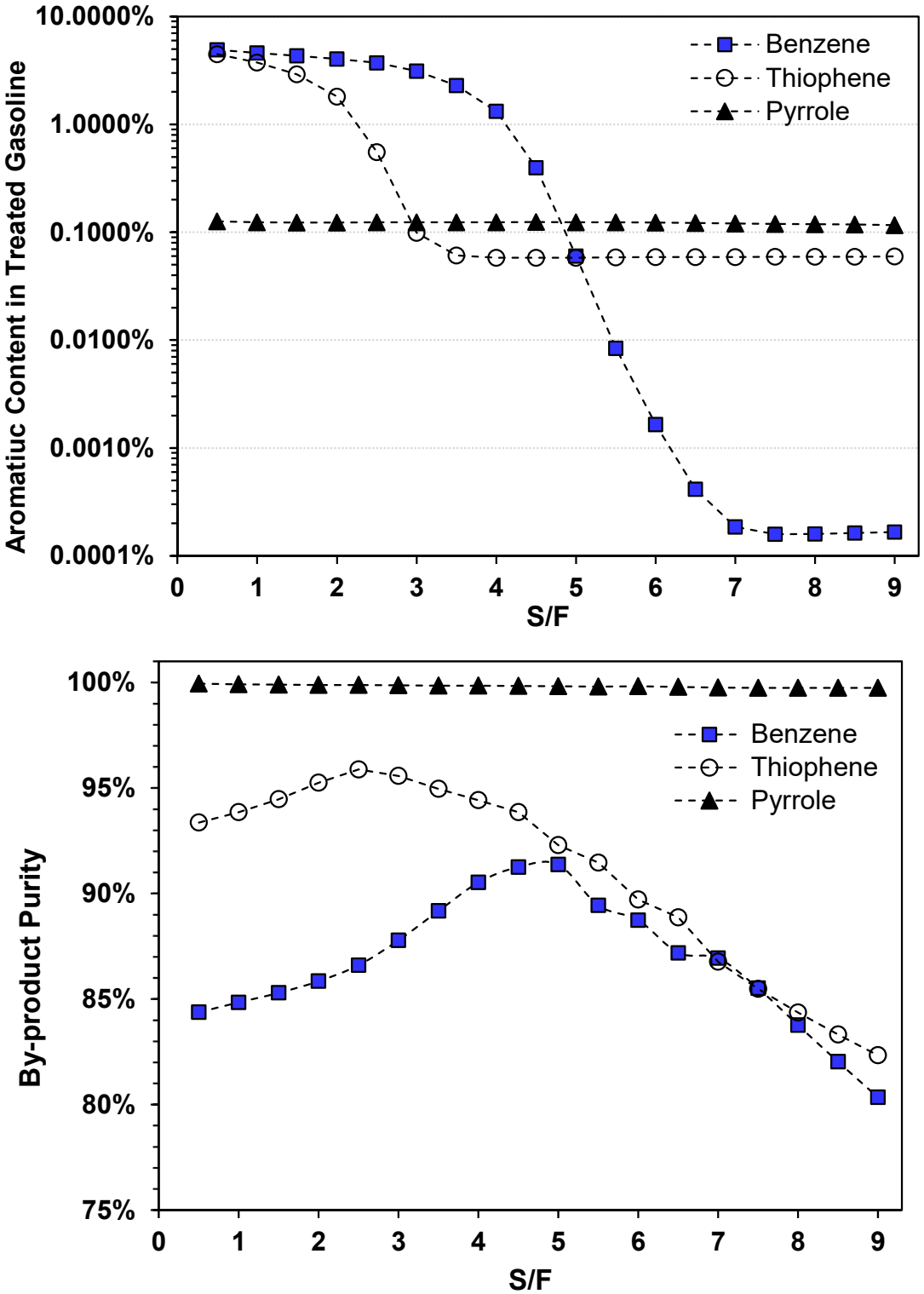

Figure 6. Benzene, pyrrole, and thiophene content in the treated gasoline and purity of the obtained by-products in the simulation of the proposed process using the COSMO-based/Aspen Plus methodology as a function of solvent-to-feed ratio.