Comparison of solvent-based affinity separation processes using Cyrene and Sulfolane for aromatic/aliphatic separations

Thomas Brouwer and Boelo Schuur*

Abstract

BACKGROUND: Vapor–liquid and liquid–liquid equilibria of unsaturated and saturated hydrocarbons with the bio-based solvent dihydrolevoglucosenone, trademarked as Cyrene, have been reported recently, aiming at the utilization of the solvent in liquid–liquid extraction (LLX) and extractive distillation (ED). In this work, for a model system comprised of methylcyclohexane (MCH) and toluene (TOL), both LLX-based and ED-based processes were compared over a wide range of compositions based on simulations in AspenPlus V10. An economic evaluation based on total annual costs was performed, and the processes using Cyrene were compared with equivalent processes using the industrial benchmark Sulfolane.

RESULTS: In the absence of literature data for Sulfolane–MCH–TOL, additional liquid–liquid extractions were done to facilitate parameter estimation for simulation. The Cyrene-based ED process was found to be more efficient than the Sulfolane-based ED process, primarily at lower (<50 mol%) TOL feed concentration, but also higher TOL feed concentrations. For LLX purposes it was found that the Cyrene-based LLX process was economically the least attractive, primarily due to the larger miscibility region of Cyrene with the hydrocarbon mixture.

CONCLUSIONS: The overall conclusion for this specific binary mixture is that LLX with Sulfolane is most economic at a TOL feed concentration of <30 mol%, while for >30 mol% the ED process with Cyrene is most economic. This process analysis showed that Cyrene is an appropriate bio-based alternative for Sulfolane as an entrainer for ED processes to separate aromatics and aliphatics.

© 2021 The Authors. Journal of Chemical Technology and Biotechnology published by John Wiley & Sons Ltd on behalf of Society of Chemical Industry (SCI).

Supporting information may be found in the online version of this article.

Keywords: liquid–liquid extraction; extractive distillation; Cyrene; dihydrolevoglucosenone; process simulation

ABBREVIATIONS

AD  azeotropic distillation
APEA  Aspen Plus Economic Analyzer
BIP  binary interaction parameter
CAPEX  capital expenditure
Cp  isobaric heat capacity (J K⁻¹ mol⁻¹)
DES  deep eutectic solvent
ED  extractive distillation
IL  ionic liquid
LLE  liquid–liquid equilibrium
LLX  liquid–liquid extraction
MCH  methylcyclohexane
NRTL  non-random two liquid
OPEX  operational expenditure
PBP  payback period
SF  solvent-to-feed
SR  solvent recovery
TAC  total annual cost
TOL  toluene
UNIQUAC  universal quasichemical
VLE  vapor–liquid equilibrium

INTRODUCTION

The fractionation of crude oils into numerous intermediates and products is practiced all around the world. Oil fractionation is an energy-intensive process due to the complexity of the feed that requires an extensive separation train. Yearly a huge amount of crude oil is produced (4.4 billion tons in 2019¹), which represents about 12.0% of the global energy usage by the petrochemical

¹ Correspondence to: B Schuur, Sustainable Process Technology Group, Process and Catalysis Engineering Cluster, Faculty of Science and Technology, University of Twente, Meander Building 221, PO Box 217, 7500 AE Enschede, The Netherlands, E-mail: b.schuur@utwente.nl

Sustainable Process Technology Group, Process and Catalysis Engineering Cluster, Faculty of Science and Technology, University of Twente, Enschede, The Netherlands

© 2021 The Authors. Journal of Chemical Technology and Biotechnology published by John Wiley & Sons Ltd on behalf of Society of Chemical Industry (SCI).

This is an open access article under the terms of the Creative Commons Attribution-NonCommercial License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited and is not used for commercial purposes.
industry.\textsuperscript{2} In our path towards a more sustainable future, the elimination of crude oil will take time, and in the short term will not be feasible as the world cannot function without carbon-based products. For the longer term, fossil-based crude oils can be replaced with bio-crude oils,\textsuperscript{3,4} but bio-crude oils also need to be refined.\textsuperscript{5,6} While in the future the use of bio-crudes might have a significant impact, further greening of traditional industrial crude processing should also be pursued to reduce environmental impacts. Part of this can be realized by increasing the energy efficiency of these processes,\textsuperscript{7} and additionally by replacing traditional solvents with bio-based solvents.\textsuperscript{8,9}

Crude oil feeds, for instance naphtha, are complex mixtures that may contain C\textsubscript{6} to C\textsubscript{8} hydrocarbons,\textsuperscript{10,11} though other composition ranges are also seen. Various hydrocarbons are close-boiling compounds, form pinch points and/or form azeotropes between each other.\textsuperscript{10,11} This is the major reason for the large energy requirements of the subsequent separation train. The motivation for separating the aromatic compounds from the aliphatic compounds apart from their individual value is that the presence of aromatic compounds hinders the production of ultralow-sulfur fuels.\textsuperscript{12} Also, the aromatic presence adds a load on the separation train and tends to foul radiation sections and transfer line exchangers.\textsuperscript{13}

Traditional distillation columns, due to the overlapping boiling ranges and azeotropes, are not able to facilitate all the required separations. Therefore solvent-based affinity processes including liquid–liquid extraction (LLX),\textsuperscript{14–16} extractive distillation (ED)\textsuperscript{17,18} and azeotropic distillation (AD)\textsuperscript{19,20} are used to enhance the relative volatility. Other processes have also been reported such as pervaporation,\textsuperscript{21,22} adsorption\textsuperscript{23,24} or using supported liquid membranes with ionic liquids (ILs)\textsuperscript{25} and polymeric membranes.\textsuperscript{26} Regarding solvent-based affinity processes, the choice of solvent has a significant effect on the overall energy efficiency of the process. The capacity, the selectivity and the boiling point of the solvent are among the selection criteria. A current state-of-the-art polar solvent used in these affinity processes is tetrahydrothiophene-1,1-dioxide or commonly known as Sulfolane.\textsuperscript{11} ILs have been widely studied as potential superior solvents,\textsuperscript{13,27–29} as shown for instance by Meindersma and de Haan\textsuperscript{13} who found that the LLX process can be markedly improved by using 4-methyl-N-butylpyridinium tetrafluoroborate. More recently, deep eutectic solvents (DESs) are stated to be an additional new class of alternative solvents.\textsuperscript{30–33} Because DESs are composite solvents and not bound by charge neutrality as seen with ILs, leaching is not necessarily the same for both (all) constituents,\textsuperscript{34,35} and the risk remains of changing the solvent composition during subsequent extraction stages.\textsuperscript{36} For this reason, a single-molecule solvent may be better suited than composite solvents such as DESs for treating complex streams such as naphtha.

In this paper, both LLX-based processes and ED-based processes are compared, because both are of relevance due to the wide range of aromatic contents found in industrial applications. The number of aromatic compounds present in a feed highly depends on the nature of the feed. For example, in ethylene crackers, the aromatic content is often 10–25%,\textsuperscript{13} while the naphtha fractions of respectively Arab and Kurdish crude oils contain about 9–15 vol%\textsuperscript{37} and 16.3 vol%\textsuperscript{38} aromatic compounds. After catalytic reforming, the subsequent reformate can contain up to 55 wt% of aromatic compounds\textsuperscript{37} and vacuum gas oil may contain 33.3 wt%.\textsuperscript{39} The last example is pyrolytic light naphtha oil from used tires, which can contain 51.8 wt% of aromatic compounds.\textsuperscript{40} This highlights the necessity of assessing processes over a wide range of aromatic content in the feed. Weissermel and Arpe\textsuperscript{19} described that for the separation of aromatic and aliphatic mixtures, three solvent-based affinity processes are preferred at different aromatic feed concentrations. LLX processes are most suitable at an aromatic feed between 20% and 65%, while ED processes are most preferred between 65% and 90%. For higher aromatic content (>90%), AD processes are preferred. They mention a lack of economically feasible processes for mixed hydrocarbon feeds containing <20% of aromatic compounds. In these processes several polar solvents have been used, such as Sulfolane,\textsuperscript{41–43} N-methylpyrrolidone,\textsuperscript{42,44} N-formylimorpholine,\textsuperscript{43,45} propylene carbonate\textsuperscript{56,47} and various glycols.\textsuperscript{58,49}

In the work reported in this paper, we compared the process performance of one of these recent bio-based solvent advances (dihydrolevogluconeose or Cyrene) with the performance of Sulfolane. The latter is one of the industrial standards for aromatics/aliphatics separations ranging from 10 to 80 mol % of aromatic content. A very limited number of binary interaction parameters are currently available for Cyrene. Hence, it was not possible to properly simulate processes of complex crude mixtures, and therefore the study was limited to a model system comprised of one aromatic compound (toluene, TOL) and one aliphatic compound (methylcyclohexane, MCH), for which the parameters have recently been reported.\textsuperscript{8,9} Both LLX and ED processes were compared, and we report here on their process configurations, simulation results and corresponding costs.

**SOLVENT-BASED AFFINITY SEPARATION PROCESS CONFIGURATIONS**

For all solvent-based separation processes, after the primary separation, a solvent regeneration is necessary. In LLX-based processes, at least two, though often even more, columns are necessary for solvent regeneration. The initial extraction of the feed with the solvent is not fully selective towards the target solute. Hence, additional fractionation is required upon solvent recovery, and, due to solvent leaching, raffinate treatment is required. Various purification strategies have been described (and patented) to purify product streams and recover solvent. For instance, de Graaf and Perga\textsuperscript{38} described a combination of two distillation columns after an extraction to recover all hydrocarbons from the solvent. A water wash is often applied to remove the leached solvent from the raffinate (aliphatic) stream. To prevent significant solvent losses, this water is returned in the solvent regeneration column, where evaporation of the water enhances the distillation efficiency due to the (steam) stripping effect of the (low-boiling) water.\textsuperscript{51–53} Though it has been reported that water can also sometimes be added into the extraction column,\textsuperscript{54} this was not done in this work.

The exact amount of unit operations, involving distillation or extraction columns or decanter vessels, and the precise connections between all columns vary among patents/processes.\textsuperscript{46,50–53} The optimal configuration may not only depend on the solvent, but also on the feed composition, feed throughput, utility costs and the surface availability at the plant. As our objective was to assess the potential of Cyrene and compare it to Sulfolane, it was our main interest to make the comparison as fair as possible. Therefore, for all processes, the process configuration was identical for both solvents. For LLX-based processes, the process

---

**References**

---
Configuration is shown in Fig. 1. A process was chosen wherein the solvent is washed from the raffinate with water. The water containing the solvent is returned to the solvent recovery (SR) column, where it is applied as strip gas to strip the TOL from the solvent. Next to the SR column, in the first distillation column, the co-extracted MCH is distilled from the solvent. The TOL leaves that column in the bottom with the solvent. The distillate purity of the first distillation column is not essential as this stream is returned to the LLX column, but it should be considered because it affects the performance of the LLX process.

The second process (Fig. 2) is designed around an ED column. Generally, for ED processes the main units are distillation columns. In the (first) ED column, the feed is introduced in the bottom section of the column, while the (high-boiling) solvent is introduced in the top section. The presence of the solvent elevates the relative volatility of the saturated hydrocarbon in the hydrocarbon mixture. In the second distillation column, the SR column, the solvent is recovered from the entrained part of the feed. The presence of several heat exchangers, coolers and pumps may be added when pressure is changed between each of the columns. Besides or due to the solvent choice, adaptations have been patented such as a phase-splitter in the condenser of the SR column when using a highly polar solvent that is not fully miscible with the aromatic compounds, and introducing side-stream withdrawal and external reflux. However, for a proper comparison as aimed at in this work, a basic ED process scheme, as can be seen in Fig. 2, was applied.

**PROCESS MODELING AND OPERATIONAL AND CAPITAL EXPENDITURES**

**Equilibrium stage model**

The processes described in the previous section were modeled using equilibrium stage models to describe the vapor–liquid equilibria (VLE) and liquid–liquid equilibria (LLE). The process simulation was subjected to the MESH (material, equilibrium, summation and heat balance) equations to uphold the conservation laws, which was performed using the software package Aspen Plus® V10. This software package is a common tool for investigating both LLX processes and ED processes. The RadFrac model was applied in all (extractive) distillation columns and the rigorous countercurrent extraction column was used in combination with the inside–outside approach of Boston and Britt for the LLX columns. All pumps were simulated with a distinct discharge pressure of either 1 or 0.08 bar dependent on the location in the process. For heat integration, heat exchangers were modeled with the Shell & Tube model and a logarithmic temperature difference of 10 K was assumed between the hot outlet stream and cold inlet stream.

**Thermodynamics and experimental data acquisition**

Accurate descriptions of VLE are essential in the simulation of each distillation operation, and in the simulations, the modified Raoult law was used to handle non-ideal behavior. The pure component vapor pressure regressions of TOL, MCH, water and........
Sulfolane were used from the Aspen Plus databank. Recent vapor pressure data of Cyrene\(^6\) (Fig. 3) were manually added and regressed following the Antoine equation. In Table 1, the Antoine coefficients of all compounds are presented.

The aim of using thermodynamic models is to most accurately describe all equilibria. This could be realized by using either the non-random two-liquid (NRTL) model\(^6\) or the universal quasi-chemical (UNIQUAC) model.\(^6\) Either model can be chosen, as they often do not outperform each other, and can correlate VLE\(^6,6\) and LLE\(^7,7\) accurately if fitted appropriately. Although Sørensen \et al.\(^7\) state that UNIQUAC is slightly preferred for ternary LLE, this is a general statement, and details on goodness of fit should be considered for each system. In this section, the VLE and LLE ternary systems are all considered, and it is discussed as to which of the models is applied for each of the simulations (thus for MCH–TOL–Sulfolane for VLE and LLE separately, and also for MCH–TOL–Cyrene for VLE and LLE separately). The MCH–TOL–Sulfolane ternary VLE were simulated with NRTL using binary interaction parameters (BIPs) present in the Aspen Plus databank (Fig. 4 and Table 2).

For the description of the MCH–TOL–Sulfolane ternary LLE, the second set of NRTL (NRTL-2) BIPs was required. In the absence of literature data, the BIPs between MCH and Sulfolane required additional experimental LLE to be fitted (Fig. 5 and Table 3). The experimental and analytical procedures are presented in the supporting information.

The MCH–TOL–Cyrene ternary VLE was also fitted to experimental data published by Brouwer and Schuur\(^8\) (Fig. 6) and simulated with NRTL using BIPs, while the BIPs of MCH–TOL were used from the Aspen Plus databank. The BIPs of MCH–Cyrene and TOL–Cyrene were fitted to the ternary VLE (Table 4).

---

**Figure 2.** Conceptual process scheme of the ED process consisting of two distillation columns. The MCH product is withdrawn from the process as the distillate of the first column, while the TOL product is withdrawn from the second column. Also, several heat exchangers and pumps are present to recover heat from the solvent recycle stream and to adjust the pressure in the various sections.

**Figure 3.** Antoine coefficient correlation of Cyrene from experimental data obtained from Baird \et al.\(^6\)

Sulfolane were used from the Aspen Plus databank. Recent vapor pressure data of Cyrene\(^6\) (Fig. 3) were manually added and regressed following the Antoine equation. In Table 1, the Antoine coefficients of all compounds are presented.

---

**Table 1.** Antoine parameters, \(P (\text{bar}) = \exp \left( A - \frac{B}{RT} + C \right) \), of Cyrene, Sulfolane, TOL, MCH and water

| Component | A      | B             | C         |
|-----------|--------|---------------|-----------|
| Cyrene    | 8.029  | 3407.318      | −97.7166  |
| Sulfolane | 9.904  | 4767.089      | −75.942   |
| TOL       | 9.948  | 3455.379      | −36.3863  |
| MCH       | 9.346  | 3068.515      | −45.1859  |
| Water     | 11.866 | 3933.389      | −41.3592  |

---

© 2021 The Authors. *Journal of Chemical Technology and Biotechnology* published by John Wiley & Sons Ltd on behalf of Society of Chemical Industry (SCI).
The UNIQUAC description of the MCH–TOL–Cyrene ternary LLE, seen in Fig. 7, was published by Brouwer and Schuur, in which also the thermodynamic consistency was shown, and the UNIQUAC correlations are presented in Table 5. Additionally, the applied interaction parameters with water are presented.

Table 2. Correlated (or applied) NRTL parameters for the MCH–TOL–Sulfolane VLE system

| Component $i$ | Component $j$ | $A_{ij}$ | $A_{ji}$ | $B_{ij}$ | $B_{ji}$ | $C_{ij}$ | Originated from |
|---------------|---------------|----------|----------|----------|----------|----------|----------------|
| MCH           | TOL           | 0        | 0        | -43.24   | 134.1    | 0.3      | APV100 VLE-IG |
| Sulfolane     | -3.473        | -1.702   | 2487     | 1270     | 0.28     | NISTV100 NIST-RK |
| TOL           | 1.398         | -0.331   | 71.41    | 223.1    | 0.3      | APV100 VLE-IG |
| MCH           | Water         | -9.473   | 9.765    | 4601     | 340.6    | 0.2      | APV100 LLE-ASPEN |
| TOL           | -7.236        | 3.988    | 4292     | 996.7    | 0.2      | APV100 VLE-IG |
| Sulfolane     | 0             | 0        | 333.4    | 432.7    | 0.6      | APV100 VLE-IG |

Interaction parameters with water are additionally given.

Figure 4. XY diagram (left) and TXY diagram (right) of the (quasi-)binary VLE diagram of MCH–TOL and Sulfolane with a SF ratio of 1 on a mass basis, including a NRTL fit the results of which are located in Table 2.

Figure 5. Ternary diagram (left) of the LLE of TOL, MCH and Sulfolane with the extract phase (open) and raffinate phase (closed), and (right) the TOL, MCH of Sulfolane at 298.15 K. The NRTL-2 parameters are located in Table 3.

The UNIQUAC description of the MCH–TOL–Cyrene ternary LLE, seen in Fig. 7, was published by Brouwer and Schuur, in which also the thermodynamic consistency was shown, and the UNIQUAC correlations are presented in Table 5. Additionally, the applied interaction parameters with water are presented.

Conclusively, all VLE are simulated using the NRTL model and the presented BIPs. While the LLE of the Sulfolane system was also simulated with the NRTL model, the simulation of the LLE of the Cyrene system was performed using UNIQUAC and corresponding BIPs which gave the best phase description.
Additional parameters, such as the density, heat capacity and enthalpy of vaporization of MCH, TOL, Sulfolane and water, were taken from the Aspen Plus databank, while the density and enthalpy of vaporization of Cyrene were manually added to the simulator.65,73 No isobaric heat capacity (C_p) of Cyrene could be found in the literature; hence it was estimated using the Joback methodology which gave C_p of 238 J mol$^{-1}$ K$^{-1}$ at 303.15 K, which is comparable to, though 34% higher than, C_p of Sulfolane, being 178 J mol$^{-1}$ K$^{-1}$ at 303.15 K.74

**Model input**

Both processes, either with Cyrene or Sulfolane, were simulated with a feed of 100 metric tons per hour, while the TOL molar fraction was varied between 10 and 80 mol% at room temperature of 293.15 K. The product specifications of MCH and TOL were both set at 99.85 wt% which coincides with industrial aromatics specifications.75 The countercurrent LLX column and the ED column were kept at 1 bar, while the additional recovery columns were at 0.08 bar. These pressures were chosen according to rigorous simulations of Qin et al.76 and enable significant heat integration between the various columns. Thermal instabilities of Sulfolane and Cyrene were not present.8

**OPEX, CAPEX and TAC**

Economic estimation of all processes was performed by assessing the operational expenditure (OPEX), the capital expenditure (CAPEX) and the total annual cost (TAC). The energy requirements of each process were provided by the Aspen Plus simulations, and a yearly operating time of 8400 h per year was used.77 The costs of various utilities are presented in Table 6. Any costs associated with specific locations were not taken into consideration.
The CAPEX was estimated using the Aspen Plus Economic Analyzer (APEA), which includes a sizing tool for distillation columns and standard overall heat transfer coefficients. No further investigations were done on the type of construction materials. APEA is not able to size extraction columns. Cost estimation of the extraction columns was therefore done by taking a conventional distillation column without reboiler and condenser and analyzing the costs for different capacities and number of stages. It was stated by Peters et al. that the cost for extraction columns can be obtained by using the assumption that the stages for the extraction column have the same spacing as in a distillation column. This was confirmed by a literature comparison, where the tray spacing of a distillation column is 0.305–0.915 m and for a rotating disk contactor is 0.6096–1.2192 m. A value of 0.6096 m is also used in the Aspen simulations for a distillation column. With this method, thus applying the costs as calculated by the APEA tool, without further reporting in detail on column heights and diameters as calculated by the APEA simulator, the cost estimation of the extraction columns was made (see Fig. S1 in the supporting information for the cost correlation). The solvent costs were determined by adding up the solvent content of each product stream and combining it with the bulk prices presented in Table 1.

The economic analysis is finalized by the TAC (€ yr⁻¹), with both CAPEX and OPEX, evaluated using Eqn (1):

\[
\text{TAC} = \text{OPEX} + \frac{\text{CAPEX}}{\text{PBP}}
\]

where a payback period (PBP) of 3 years is applied.

RESULTS

To explain the interpretation of the simulation results, in the first two following subsections the LLX and ED processes with both solvents are elaborated for a feed containing 40 mol% TOL. All other simulations with variations in the feed composition were done similarly. First, the LLX process is discussed, where the effects of the solvent-to-feed (SF) ratio, the water-to-extract ratio, the UNIQUAC fit parameters are located in Table 5.

Table 5. Correlated (or applied) UNIQUAC parameters for the MCH-TOL-Cyrene system

| Component i | Component j | A_i | A_j | B_i | B_j | Originated from |
|-------------|-------------|-----|-----|-----|-----|----------------|
| MCH         | TOL         | 0   | 0   | -191.0 | 171.5 | 9              |
| TOL         | Cyrene      | 4.587 | -2.627 | -1749 | 773.7 | 9              |
| MCH         | Water       | 2.708 | -4.999 | -772.6 | 1463 | 9              |
| TOL         | Water       | 0   | 0   | -1208 | -534.02 | APV100 LLE-LIT |
| Cyrene      | Water       | 0   | 0   | -950.6 | -350.21 | APV100 LLE-LIT |

Interaction parameters with water are additionally given.

Table 6. Specifications of used utilities and associated costs

| Utility                  | Costs | Ref |
|--------------------------|-------|-----|
| Chilled cooling water    | 4.50 € GJ⁻¹ | 78   |
| Medium pressure steam    | 11.34 € GJ⁻¹ | 78   |
| Electricity              | 18.97 € GJ⁻¹ | 79   |
| Sulfolane bulk price     | 2.55 € kg⁻¹⁻¹ | 80   |
| Cyrene bulk price        | 2.00 € kg⁻¹⁻¹ | 81   |

a Conversion from $ to € of 0.84976 of 20 October 2020 was used.
b Bulk price of Sulfolane may vary between 2500 and 3500 $ ton⁻¹; 3000 $ ton⁻¹ was used.
c Bulk price of Cyrene was stated by Krishna et al.
the number of extraction stages, the effect of reflux ratios in the recovery columns and the (water) feed location are assessed. The OPEX of the optimized configuration is also discussed. Second, a similar assessment is done for the ED process, where the SF ratio, the reflux ratios, the (solvent) feed location and the OPEX are assessed. Third, the TAC (and all OPEX) is calculated and compared for all processes with a 10 to 80 mol% aromatic content range.

LLX process
The LLX process includes two extraction operations, namely the main LLX column where the aromatic compound is extracted from the hydrocarbon feed and the washing step where the leached solvent is washed from the raffinate stream. First, the influence of the SF ratio in the LLX column and the number of equilibrium stages is assessed in Fig. 8(a). Second, the impact of variation of the reflux ratio and the location of the feed stage in the first distillation column is displayed in Fig. 9. Third, the impact of the reflux ratio and the water feed stage on the performance in the second distillation column was studied (Fig. 10).

In the LLX column, the TOL impurity should be low enough to realize the MCH product specification. It can be seen that both the SF ratio and the number of equilibrium trays affect the TOL impurity (maximum of $1.5 \times 10^{-3}$ mol%). It can be seen that with only five equilibrium stages, it is not possible to reach the allowed maximum TOL impurity within the simulated SF ratio range for the Sulfolane process. Although with a SF ratio range higher than 3, it is possible for the Cyrene process and even higher SF ranges based on the observed trend are expected. It can be seen that a smaller amount of Cyrene is required compared to Sulfolane, which is due to the larger aromatic dissolving capacity of Cyrene. The amount of solvent can be reduced by increasing the number of equilibrium stages. This will also affect the first distillation column where the co-extracted MCH needs to be distilled. In any case, a certain amount of solvent is leached into the raffinate stream, which is easily recovered by the wash column, as both Sulfolane and Cyrene are fully miscible in water, in contrast to MCH which is highly immiscible with water.

The water-to-feed ratio directly impacts the second distillation column, as this (contaminated) water is reused as a stripping agent.$^{41,86}$ The solvent-contaminated water from the water wash is sent to the second distillation column, where it evaporates to steam and strips the TOL from the solvent. This allows an efficient separation, and the water can be collected via a phase separation step after the condenser. As can be seen in Fig. 8(b), the amount of water used in the wash column also directly impacts the second recovery column, where the aromatic compounds are stripped with steam. It can be seen that only a small amount of water is required in the wash column to remove the leached Sulfolane or Cyrene. This is in accordance with the findings of Lee and Coombs$^{86}$ and Wang et al.$^{79}$ who determined that at least respectively 1 and 0.89–1.1 wt% of water in Sulfolane was required for adequate stripping of the aromatic compounds.

The influence of the process conditions on removal of the co-extracted MCH in the first distillation column was investigated. From Fig. 9(a), it is clear that in the simulations with six stages the MCH impurity specifications of the bottom stream are never met, and more stages are needed. With eight stages it appears possible for both solvents, although in the plotted area for Sulfolane the specification is just not met at $R = 0.30$. An important conclusion from these data is that the purity in the bottom stream is largely independent of the reflux ratio. This is indicative of the small amount of co-extracted MCH (and some TOL) which is distilled over the top. In Fig. 9(b) it can be seen that the feed location has a significant influence on the MCH impurity in the bottom streams. The feed should be near the top of the column, this allowing sufficient MCH removal.

In Fig. 10(a) it can be seen that Sulfolane requires a lower minimum reflux ratio than Cyrene, which is a consequence of the lower volatility of Sulfolane. Secondly, in Fig. 10(b), the optimal feed location of the stripping water is not very strict. However, the stripping water should not be introduced near the top or bottom of the column as this would diminish the TOL purity below specification. Near the bottom, the temperature is significantly higher and causes the water to be mostly in the vapor phase which diminishes its repulsive interactions towards the hydrocarbons in the liquid phase. Also, it can be seen that only six equilibrium stages are inadequate when using Cyrene as a solvent. Eventually, the amount of water is kept as low as possible without compromising the stripping ability. This is required as the energy penalty of evaporating the water needs to be minimized.

![Figure 8](image-url) Effect of (a) SF (molar) ratio of LLX column and (b) water-to-feed ratio in the wash column located after the LLX column with a SF ratio of 3.5 and with a 40 mol% aromatic feed and Sulfolane or Cyrene as solvent.
In the case of eight equilibrium stages, the vapor concentration profiles in both distillation columns are presented for both solvents in Fig. 11. The recycling back to the LLX column of the co-extracted MCH as distillate is seen in Figs 11(a) and (b), which simultaneously purifies the bottom fraction containing afterward solely TOL and solvent. This first distillation column operates at a temperature for which the solvent largely remains liquid. The distillate contains a fraction of TOL, a consequence of a low reflux ratio, which minimizes the reboiler duty. Also, this is of no consequence for the process as the distillate is returned to the LLX column where the TOL is again extracted to the solvent phase. The TOL fraction in the Sulfolane-based process is much higher, which is required to lower the impact of the pinch point at higher MCH fractions. Cyrene-based processes do not have this problem, due to less strong repulsive interactions towards the hydrocarbons than observed with Sulfolane, and allow for a higher MCH purity as a top product.

In Figs 11(c) and (d) the concentration profiles are plotted for the second distillation column for Cyrene and Sulfolane, respectively. The addition of the stripping water (vapor) is seen through the concentration profile of water in the vapor phase. This stripping water is contaminated with the leached solvent from the LLX raffinate stream. The water strips the TOL from the solvent and a distillate containing water and TOL which are separated via a phase splitter in the condenser. Although the molar fraction of water in the vapor phase is considerable, it is still comparatively a small weight fraction. For both the Cyrene process and Sulfolane process a comparable amount of steam is introduced in the SR columns of both processes as strip gas, and due to the higher temperature in the Sulfolane-based process, a larger molar vapor fraction of water is observed. A high solvent purity is required at the bottom as this is returned to the LLX column and unwanted solute recycling is prevented. Although water in the solvent recycle stream is not necessarily detrimental for the process, the water...
Figure 11. (a) First distillation column of the Cyrene-based LLX process (feed: 15 mol% MCH, 15 mol% TOL, 70 mol% Cyrene, SF ratio of 2.5, reflux ratio of 0.1); (b) first distillation column of the Sulfolane-based LLX process (feed: 4.1 mol% MCH, 13 mol% TOL, 82 mol% Sulfolane, SF ratio of 3.25, reflux ratio of 0.62); (c) second distillation column of the Cyrene-based LLX process (feed: trace MCH, 14 mol% TOL, 86 mol% Cyrene, SF ratio of 2.5, reflux ratio of 1.4, 2.7 mol% (0.39 wt.%) water relative to Cyrene, stripping water contains 9.0 mol% Cyrene); (d) second distillation column of the Sulfolane-based LLX process (feed: trace MCH, 11 mol% TOL, 89 mol% Sulfolane, SF ratio of 3.25, reflux ratio of 0.7, 3.7 mol% (0.55 wt%) water relative to Sulfolane, stripping water contains 0.9 mol% Sulfolane).

Figure 12. OPEX of the LLX processes with a range of aromatic contents in the feed: (a) Cyrene; (b) Sulfolane.
fraction in the bottom stage of the SR column is low, due to the much lower boiling point of water compared to either solvent.

**OPEX analysis**

In Fig. 12 the OPEX of all LLX processes is shown. A distinction is made between costs associated with heating, cooling, electrical duty and solvent losses. Overall, the OPEX of the Cyrene-based LLX process is significantly higher than that of the Sulfolane-based LLX process. This is due to primarily the lower selectivity towards TOL. This causes additional load on the first distillation column which recovers the co-extracted MCH and the boiling point of Cyrene is lower than that of Sulfolane, which causes higher reflux requirements in the recovery column. Nevertheless, less Cyrene is required than Sulfolane (due to a larger capacity towards TOL) to extract all TOL. The larger capacity also causes a larger miscibility region of Cyrene with the TOL–MCH mixture and a limited operation region up to 40 mol% of TOL in the feed. It is therefore only possible as higher aromatic concentrations will not cause a phase split which makes LLX impossible. A clear trend is observed regarding the OPEX of the Sulfolane-based LLX process with a decreasing OPEX from 80 mol% to 50 mol% TOL in the feed. The costs reach a minimum of around 50 mol% of TOL in the feed, and stay very similar to 20 mol%, under which it increases again. This is due to the fact the distillation costs within the process are equally distributed between both distillation columns. At lower aromatic fractions, the load is placed more on the first distillation column, whereas at a higher aromatic fraction the load is shifted towards the aromatic product recovery from the solvent in the second distillation column.

**ED process**

The ED process is simpler than the LLX process, as there are only two main distillation columns. First, the effects of the SF ratio and the number of equilibrium stages are assessed in the first distillation column, or the ED column, in Fig. 13. Second, the effect of the reflux ratio is evaluated in Fig. 14. Third, the effects of the feed location of the hydrocarbon stream and of the solvent stream in the ED column are assessed in Figs 15 and 16. Last, the reflux ratio and the feed location of the second distillation column are assessed in Fig. 17.

In the ED column, MCH is separated from the TOL–solvent mixture. Here the key parameters are the MCH impurity in the bottom stream and the MCH purity in the top stream. As can be seen in Fig. 13, an increasing number of equilibrium stages allows for a deeper removal of MCH, thereby lowering the MCH impurity in the bottom stream with less solvent to achieve the maximum allowed MCH impurity in the bottom stream. Cyrene is seen to require less solvent to obtain the desired MCH purity than Sulfolane, due to the lack of pinch point in the ternary VLE behavior of Cyrene–TOL–MCH.6

It can be seen in Fig. 14 that a lower reflux ratio can be used in the Sulfolane system compared to the Cyrene system. This is a consequence of the higher SF ratio used for the Sulfolane system. The SF ratio and the reflux ratio in the Cyrene system appear to have a much smaller effect compared to the Sulfolane system, indicating that a much smaller amount of equilibrium stages can be used for the Cyrene system. This is likely due to the fact that a higher SF ratio in the Sulfolane system strongly affects the severity of the pinch point, which does not occur in the Cyrene system. In general, the MCH purity specification is obtained, and the MCH impurity in the bottom stream is the key parameter to consider, as this directly influences the TOL purity in the subsequent column.

Overall, the hydrocarbon feed should not be introduced close to the top as it reduces the rectifying ability. Both solvents require a feed location of at least lower than the 15th stage. This is necessary to not only obtain MCH product purity, but also to allow sufficient removal of MCH from the bottom stream. An introduction of the hydrocarbon too low in the column will result in insufficient removal of MCH from the bottom stream, which consequently will result in an inability to purify the TOL product in the subsequent column.

Besides the hydrocarbon feed location, also the location at which the solvent is introduced in the ED column is essential. The effect of this location is seen in Fig. 16. Similar trends are observed as seen in Fig. 15; hence the introduction of the solvent too high up the column will reduce the MCH purity in the top to below specification. While adding the solvent too low in the column will result in insufficient MCH removal from the bottom stream and again adversely affect the possible TOL purity in the subsequent recovery column.

![Figure 13. Effect of SF (molar) ratio in the (first) ED column on (a) MCH purity in the top stream and (b) MCH impurity in the bottom stream with a 40 mol % aromatic feed using Sulfolane or Cyrene as a solvent and a reflux ratio of 2.0.](image-url)
In the (second) distillation column or SR column, the TOL purity is the key parameter. In Fig. 17(a) the minimal reflux ratio can be seen to be slightly dependent on the number of equilibrium stages. This indicates that the relative volatility of the solvent is much lower than that of the hydrocarbons. Also, fewer equilibrium stages are required compared to the ED column. This again indicates that the separation in the SR column is less difficult, which is expected based on the much larger relative volatility between solvent and TOL than between TOL and MCH. It can be seen that the Cyrene-based ED process requires more equilibrium stages and a larger reflux ratio in the SR column. This is due to the higher volatility of Cyrene compared to Sulfolane. In Fig. 17(b) it can be seen that the feed location follows the same trends as seen before. A feed entrance too high up the column reduces the TOL purity and may even be insufficient to achieve the required specification.

Overall, an interplay between sufficient solvent to allow an efficient MCH separation in the ED column and a minimization of the energy penalty in the SR column is required. In Fig. 18 an example of the concentration profiles in each column is seen. In the ED column, it is seen that the heavy boiling solvent, which is added in the top section of the ED column, remains in the liquid phase, while the top product reaches the targeted MCH purity. The VLE of MCH and TOL with Sulfolane present exhibits a pinch point hence more equilibrium trays are required to obtain the MCH specification. In the SR column, TOL is distilled from the solvent without any stripping water. Also in this process, the purity of the recycled solvent is high to prevent unwanted solute recycling.

**OPEX analysis**

In Fig. 19 the OPEX of all ED processes is shown. Also, in this case, a distinction is made between costs associated with heating, cooling, electrical duty and solvent losses. As can be seen, both Cyrene-based and Sulfolane-based processes operate at a minimum OPEX around an equimolar MCH–TOL feed mixture. This minimum was also seen in the LLX-based process, and is again due to the load being shared equally in this case between both distillation columns. Also, the operation window of the Cyrene-based process is larger, as it includes a TOL feed composition of

---

**Figure 14.** Effect of reflux ratio in the (first) ED column on (a) MCH purity in the top stream and (b) MCH impurity in the bottom stream with a 40 mol% aromatic feed using Sulfolane or Cyrene as solvent and respectively SF ratio of 5.0 and 2.0.

**Figure 15.** Effect of feed location in the (first) ED column on (a) MCH purity in the top stream and (b) MCH impurity in the bottom stream with a 40 mol% aromatic feed using Sulfolane or Cyrene as a solvent and respectively SF ratio of 5.0 and 2.0 and respectively a reflux ratio of 0.5 and 1.0.

---

www.soci.org T Brouwer, B Schuur

© 2021 The Authors. J Chem Technol Biotechnol 2021

Journal of Chemical Technology and Biotechnology published by John Wiley & Sons Ltd on behalf of Society of Chemical Industry (SCI).
10 mol%, due to the larger miscibility region of Cyrene compared to Sulfolane.

The larger miscibility was detrimental in the LLX-based process, though it is an advantage in the ED process as it is not limited by the intermolecular interactions at lower TOL concentrations. In both processes, the OPEX increases at higher (>60 mol%) TOL concentration and low concentration (<60 mol%). Increasing the amount of MCH present increases the load on the ED columns, as higher refluxes are required to obtain the required target purity of MCH. Increasing the amount of TOL increases the load on the SR column, as more TOL needs to be stripped from the solvent which also requires higher reflux ratios. Overall comparing both processes, a similar trend can be recognized in the OPEX, although a lower OPEX is seen for the Cyrene-based process, which is a combined result from the lower temperatures required in both columns and the absence of the detrimental pinch point present only in the ternary Sulfolane–MCH–TOL mixture.

**TAC comparison**

In this comparison of the costs related to the entire process, both the OPEX and the CAPEX are taken into consideration in the TAC. A detailed equipment list and associated costs for each process are presented in Tables S1–S4 in the supporting information. The CAPEX differences between the Cyrene-based LLX process (3.11–4.67 M€ yr\(^{-1}\) or 30.11–34.12 € ton\(_{feed}\)\(^{-1}\) yr\(^{-1}\)) and Sulfolane-based LLX process (1.56–2.27 M€ yr\(^{-1}\) or 26.99–35.28 € ton\(_{feed}\)\(^{-1}\) yr\(^{-1}\)) are significant. Cyrene exhibits unfavorable miscibility which increases the solvent volume. The CAPEX differences between the Cyrene-based ED process (1.41–2.25 M€ yr\(^{-1}\) or 20.84–24.77 € ton\(_{feed}\)\(^{-1}\) yr\(^{-1}\)) and Sulfolane-based ED process (1.58–2.68 M€ yr\(^{-1}\) or 22.7–25.6 € ton\(_{feed}\)\(^{-1}\) yr\(^{-1}\)) are not very large, although present due to a variance in equilibrium stages, in temperatures and in solvent volume.

As can be seen in Fig. 20 where all processes are compared, a Cyrene-based LLX process is economically the least attractive. The LLX process with Sulfolane and also ED processes with both

---

**Figure 16.** Effect of solvent feed location in the (first) ED column on (a) MCH purity in the top stream and (b) MCH impurity in the bottom stream with a 40 mol% aromatic feed using Sulfolane or Cyrene as a solvent and respectively SF ratio of 5.0 and 2.0 and respectively a reflux ratio of 0.5 and 1.0.

**Figure 17.** (a) Effect of reflux ratio and (b) feed location in SR column on TOL purity in the top stream with a 40 mol% aromatic feed using Sulfolane or Cyrene as a solvent and respectively SF ratio of 5.0 and 2.0 and in (b) a reflux ratio of 1.5.
Figure 18. (a) The (first) column of the Cyrene-based ED process (feed: 60 mol% MCH, 40 mol% TOL, SF ratio of 1.6, reflux ratio of 0.27), (b) the (first) column with of the Sulfolane-based ED process (feed: 60 mol% MCH, 40 mol% TOL, SF ratio of 3.5, reflux ratio of 1.6), (c) the (second) distillation column of the Cyrene-based ED process (feed: trace MCH, 20 mol% TOL, 80 mol% Cyrene, reflux ratio of 0.78) and (d) the (second) distillation column of the Sulfolane-based ED process (feed: trace MCH, 10 mol% TOL, 90 mol% Sulfolane, reflux ratio of 0.8).

Figure 19. OPEX of the LLX processes with a range of aromatic contents in the feed: (a) Cyrene; (b) Sulfolane.
The future of petrochemicals. Paris. https://www.iea.org/reports/the-future-of-petrochemicals.

3 Dimitriadi A and Bezergianni S, Hydrothermal liquefaction of various biomass and waste feedstocks for biocrude production: a state of the art review. Renew Sustain Energy Rev 68:113–125 (2017).

4 Oudenhoven S, Westerhof RJM, Aldenkamp N, Brilman DWF and Kersten SR, Demineralization of wood using wood-derivated acid: towards a selective pyrolysis process for fuel and chemicals production. J Anal Appl Pyrolysis 103:112–118 (2013).

5 Westerhof RJ, Brilman DWF, Garcia-Perez M, Aaldenkamp N, Brilman DWF and Kersten SR, Aromatic extraction from pyrolytic sugars using ionic liquid to enhance sugar fermentability. Bioresour Technol 216:12–18 (2016).

6 Li X, Luque-Moreno LC, Oudenhoven SR, Rehmann L, Kersten SR and Schuur B, Aromatics extraction from pyrolytic sugars using ionic liquid to enhance sugar fermentability. Bioresour Technol 216:12–18 (2016).

7 Agrawal R and Gooty RT, Misconceptions about efficiency and maturity of distillation. AIChE J 66:16294 (2020).

8 Brouwer T and Schuur B, Bio-based solvents as entrainers for extractive distillation in aromatic/aliphatic and olefin/paraffin separation. Green Chem 22:5369–5375 (2020).

9 Brouwer T and Schuur B, Dihydrolevoglucosenone (Cyrene), a bio-based solvent for liquid-liquid extraction applications. ACS Sustain Chem Eng 8:14807–14817 (2020).

10 Abushirewib F, Elakrami H and Emtri M, Recovery of aromatics from pyrolysis gasoline by conventional and energy-integrated extractive distillation. Comput Aided Chem Eng 24:24107–1076 (2007).

11 Blahusiak M, Kiss AA, Babic K, Kersten SR, Bargeman G and Schuur B, Insights into the selection and design of fluid separation processes. Sep Purif Technol 194:301–318 (2018).

12 Sharma M, Sharma P and Kim JN, Solvent extraction of aromatic components from petroleum derived fluids: a perspective review. RSC Adv 3:10103–10126 (2013).

13 Meindersma GW and de Haan AB, Conceptual process design for aromatics/aliphatie separation with ionic liquids. Chem Eng Res Des 86:745–752 (2008).

14 Meindersma GW, Hansmeier AR and de Haan AB, Ionic liquids for aromatics extraction. Present status and future outlook. Ind Eng Chem Res 49:7530–7540 (2010).

ACKNOWLEDGEMENTS
The work reported is an ISPT (Institute for Sustainable Process Technology) project (TEEI314006/B/20-07), co-funded by Top-sector Energy by the Dutch Ministry of Economic Affairs and Climate Policy. We also acknowledge Esther Slouwerhof and Remko van Gestel for their work on this subject.

SUPPORTING INFORMATION
Supporting information may be found in the online version of this article.
15 Meindersma W, Onink F, Hansmeier AR and de Haan AB, Long term pilot plant experience on aromatics extraction with ionic liquids. Sep Sci Technol 47:337–345 (2012).
16 Onink F, Drum C, Meindersma GW, Bart H-J and de Haan AB, Hydrodynamic behavior analysis of a rotating disc contactor for aromatics extraction with 4-methyl-buty1- pyridinium BF4 by CFD. Chem Eng J 160:51–58 (2010).
17 Navarro P, de Diego García I, Larribá M, Delgado-Mellado N, Ayuso M, Moreno D et al, Deaeromatization of pyrolysis gasoline by extractive distillation with 1-ethyl-3-methylimidazolium tri-cyanomethanide. Fuel Process Technol 195:106156 (2019).
18 Zhang Y, Yang Y, Chen F, Liu S, Zhao L, Gao J et al, Research on a dual solvent to separate olefinic-alkene, aldehyde from high fluid catalytic cracking naphtha. Ind Eng Chem Res 57:4064 (2018).
19 Weissermel K and Arpe H-J, Industrial Organic Chemistry. Wiley-VCH, Weinheim, p. 446 (1997).
20 Widagdo S and Seider WD, Journal review. Azeotropic distillation. AIChE J 42:96–130 (1996).
21 Pitman F, Staudt-Bickel C, Hess S and Lichtenthaler RN, Polymeric membranes for aromatic/alkiphatic separation processes. Chem Phys Chem 3:856–862 (2002).
22 Matuszewskii H and Scheller U, MSE-modified membranes in organophilic pervaporation for aromatics/alkiphatics separation. Desalination 224:124–131 (2008).
23 Dessau RM, inventor; ExxonMobil Oil Corp, assignee. Selective sorption of linear aliphatic compounds by zeolites. US Patent US4517402A (1995).
24 Takahashi A, Yang FH and Yang RT, Aromatics/alkiphatics separation by adsorption: new sorbents for selective aromatics adsorption by \( \pi \)-complexation. Ind Eng Chem Res 39:3856–3867 (2000).
25 Matsumoto M, Inomoto Y and Kondo K, Selective separation of aromatic hydrocarbons through supported liquid membranes based on ionic liquids. J Membr Sci 246:77–81 (2005).
26 Partridge RD, Pfeffer DG, Dalrymple DC, Weissman W, inventors; ExxonMobil Research and Engineering Co, assignee. Polymer membrane for separating aromatic and aliphatic compounds. US Patent US7584212B2 (2010).
27 Arce A, Earle MJ, Rodríguez H and Seddon KR, Separation of aromatic hydrocarbons from alkanes using the ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethyl sulfonyl) amide. Green Chem 9:70–74 (2007).
28 Arce A, Earle MJ, Rodríguez H, Seddon KR and Soto A, 1-Ethyl-3-methylimidazolium bis(trifluoromethyl sulfonyl) amide as solvent for the separation of aromatic and aliphatic hydrocarbons by liquid extraction: extension to C 7- and C 8-alkanes. Green Chem 10:1294–1300 (2008).
29 Meindersma GW, Podt AJ and de Haan AB, Ternary liquid–liquid equilibrium for mixtures of toluene + n-heptane + an ionic liquid. Fluid Phase Equilib 247:158–168 (2006).
30 Hadi-Kali MK, Salleh Z, Ali E, Khan R and Hashim MA, Separation of aromatic and aliphatic hydrocarbons using deep eutectic solvents: a critical review. Fluid Phase Equilib 386:152–167 (2012).
31 Mulyono S, Hizaddin HF, Alnashef IM, Hashim MA, Fakeeha AH and Hadj-Kali MK, Separation of BTEX aromatics from n-octane using a (tetrabutylammonium) chloride modified perivaporation for aromatics/aliphatics separation. Fuel 351:124–128 (2021).
32 Huang J, Wang L, Liu X, Le X and Zhang K, A new sulfolane extractive distillation process and optimization for better energy utilization. Chem Eng Process 128:80–95 (2018).
33 Krishna R, Extraction of aromatics from 63-69°C naphtha fraction for food grade hexaneBASE production using Sulpholane and NMP as selective cracking media. Energy Fuel 32:607–608 (2018).
34 Mahmodhi J and Lotfollahi MN, Liquid + liquid equilibration of (sulfolane + benzene + n-hexane), (N-formylmorpholine + benzene + n-hexane), and (sulfolane + N-formylmorpholine + benzene + n-hexane) at temperatures ranging from (298.15 to 318.15) K: experimental results and correlation. J Chem Thermodyn 42:466–471 (2010).
35 Muller E, Enkheim B, John KP, inventors; Metalgessellschaft AG, assignee. Process of separating pure aromatic hydrocarbons from hydrocarbon mixtures. US Patent US3591940A, 1971.
36 Zhu H, Shi XI-J and Zhou W-Y, Process simulation and parameter optimization of separating aromatic and non-aromatics by extractive distillation with \( \mathrm{N} \)-formylmorpholine. J East China Univ Sci Technol 34:309–331 (2008).
37 Adolph S, Martin S, Von KK, inventors; Beazer East Inc, assignee. Recovery of aromatic hydrocarbon by extractive distillation with anhydrous liquid propylene carbonate. US Patent US3227632A, 1966.
38 Salem ABS and Hamad EZ, Liquid-liquid equilibrium of the five component system of \( \mathrm{n} \)-hexane–\( \mathrm{n} \)-heptane–toluene–o-xylene–propylene carbonate. Fluid Phase Equilib 108:231–241 (1995).
39 Somek G, Kubek D, Kossem A, inventors; Katalistiks International Inc, assignee. Process for the separation of aromatic hydrocarbons from a mixed hydrocarbon feedstock. US Patent US3714033A, 1973.
40 Somek G and Friedlander BO, Tetraethylene glycol—a superior solvent for aromatics extraction, in Refining Petroleum for Chemicals. Advances in Chemistry, Vol. 97. American Chemical Society, Washington, DC, pp. 228–241 (1999).
41 de Graff RR, Perga MW, inventors; Universal Oil Products Co, assignee. Method for aromatic hydrocarbon recovery. US Patent US3466346A, 1969.
42 Thompson HL, inventor; Universal Oil Products Co, assignee. Process for the extraction and recovery of aromatic hydrocarbons. US Patent US3544453A, 1970.
43 Morin RD, Fishel JB, Bearse AE, inventors; Ohio Oil Co, assignee. Separation of aromatic hydrocarbons from non-aromatic hydrocarbons utilizing a lactam-water solvent. US Patent US2933448A, 1960.
44 Jones EA, Broughton DB, inventors; Universal Oil Products Co, assignee. Solvent extraction process for recovery of aromatic hydrocarbons. US Patent US3173966A, 1965.
45 Pleuss R, Schulze M, Ribot S, Hewals W, inventors; Knupp Koppers GmbH, assignee. Process for recovering highly pure aromatics from a mixture of aromatics and non-aromatics. US Patent US5408135A, 1998.
46 Gentry JC, Berg L, McIntyre JC, Wytcherley RW, inventors; GTC Technology Inc, assignee. Process to recover benzene from mixed hydrocarbons by extractive distillation. US Patent US5329924A, 1995.
47 Furrhacker TD, inventor; Tex Petroleum Technologies Corp, assignee. Method of purifying unsaturated hydrocarbons by extractive distillation with side stream removal and solvent mix. US Patent US3681202A, 1972.
48 Cline B, inventor; Shell Oil Co., assignee. Extractive distillation of aromatic compounds. US Patent US2981661A, 1961.
49 Larribá M, de Riva J, Navarro P, Moreno D, Delgado-Mellado N, García J et al, COSMO-based/Aspen Plus process simulation of the aromatic extraction from pyrolysis gasoline using the ([4Empy][NTf2])\([ \text{emim} ]\) (DCA) ionic liquid mixture. Sep Purif Technol 190:211–227 (2018).
50 Reyhanitash E, Brouwer T, Kersten SRA, van der Ham AGJ and Schuur B, Liquid − liquid extraction-based process concepts for recovery of carboxylic acids from aqueous streams: evaluated for dilute streams. Chem Eng Res Des 137:510–533 (2018).
51 Fouladvand MT, Asadi J and Lotfollahi MN, Simulation and optimization of aromatic extraction from lube oil cuts by liquid-liquid extraction. Chem Eng Res Des 165:118–128 (2021).
61 Díaz I, Palomar J, Rodríguez M, de Riva J, Ferro V and González EJ, Ionic liquids as entrainers for the separation of aromatic–aliphatic hydrocarbon mixtures by extractive distillation. *Chem Eng Res Des* **115**: 382–393 (2016).

62 Wang Q, Zhang B, He C, He C and Chen Q, Optimal design of a new aromatic extractive distillation process aided by a co-solvent mixture. *Energy Procedia* **105**: 4927–4934 (2017).

63 Boston J and Britt H, A radically different formulation and solution of the single-stage flash problem. *Comput Chem Eng* **2**: 109–122 (1978).

64 Baird Z, Uusi-Kyyny P, Pokki J-P, Pedegert E and Alopaeus V, Vapor pressures, densities, and PC-SAFT parameters for 11 bio-compounds. *Int J Thermophys* **40**: 1–36 (2019).

65 Renon H and Prausnitz JM, Local compositions in thermodynamic excess functions for liquid mixtures. *AIChE J* **14**: 135–144 (1968).

66 Fredenslund A, Jones RL and Prausnitz JM, Group-contribution estimation of activity coefficients in nonideal liquid mixtures. *AIChE J* **21**: 1086–1099 (1975).

67 Döker M and Gmehling J, Measurement and prediction of vapor–liquid equilibria of ternary systems containing ionic liquids. *Fluid Phase Equilib* **227**: 255–266 (2005).

68 Tu C-H, Wu Y-S and Liu T-L, Isobaric vapor-liquid equilibria of the methanol, methyl acetate and methyl acrylate system at atmospheric pressure. *Fluid Phase Equilib* **135**: 97–108 (1997).

69 Alkandary JA, Aljimaz AS, Fandary M and Fahim MA, Liquid–liquid equilibria of water + MTBE + reformate. *Fluid Phase Equilib* **187**: 131–138 (2001).

70 Al-Muhtaseb SA and Fahim MA, Phase equilibria of the ternary system water/acetic acid/2-pentanol. *Fluid Phase Equilib* **123**: 189–203 (1996).

71 Misefari A, Investigation of the Spectroscopic, Chemical and Physical Properties of Cyrene and Its Hydrate. University of York, York (2017).

72 Dortmund Databank 2020.

73 Miseñiar, Investigation of the Spectroscopic, Chemical and Physical Properties of Cyrene and Its Hydrate. University of York, York (2017).

74 portland Databank 2020.

75 Chao P-H, Lin H-W, Chen C-H, Wang P-Y, Chen Y-F, Sei H-T et al., Precoking selectivation for improving benzene product purity in heavy aromatic transalkylation. *Appl Catal A* **335**: 15–19 (2008).

76 Qin J, Ye Q, Xiong X and Li N, Control of benzene–cyclohexane separation system via extractive distillation using sulfolane as entrainer. *Ind Eng Chem Res* **52**: 10754–10766 (2013).

77 Jongmans MTG, Hermens E, Rajmakers M, Maassen JW, Schuur B and de Haan AB, Conceptual process design of extractive distillation processes for ethylbenzene/styrene separation. *Chem Eng Res Des* **90**: 2086–2100 (2012).

78 Towler G and Sinnott R, *Chemical Engineering Design: Principles, Practice and Economics of Plant and Process Design*. Elsevier, London (2012).

79 Electricity: US Energy Information Administration; 2020. https://www.eia.gov/energyexplained/electricity/prices-and-factors-affecting-prices.php.

80 Alibaba. Sulfolane Bulk Price Alibaba: Alibaba; 2020.

81 Krishna SH, Huang K, Barnett KJ, He J, Maravelias CT, Dumesic JA et al., Oxygenated commodity chemicals from chemo-catalytic conversion of biomass derived heterocycles. *AIChE J* **64**: 1910–1922 (2018).

82 Peters MS, Timmerhaus KD, West RE, Timmerhaus K and West R, *Plant Design and Economics of Chemical Engineers*. McGraw-Hill, New York (1968).

83 Li L, Tu Y, Sun L, Hou Y, Zhu M, Guo L et al., Enhanced efficient extractive distillation by combining heat-integrated technology and intermediate heating. *Ind Eng Chem Res* **55**: 8837–8847 (2016).

84 Luyben WL and Chien I-L, *Design and Control of Distillation Systems for Separating Azeotropes*. John Wiley, New York (2011).

85 Knight JR and Doherty MF, Optimal design and synthesis of homgeneous azeotropic distillation sequences. *Ind Eng Chem Res* **28**: 564–572 (1989).

86 Lee FM and Coombs DM, Two-liquid-phase extractive distillation for aromatics recovery. *Ind Eng Chem Res* **26**: 564–573 (1987).

87 Fandary M, Aly G, Fahim M and Mumford C, Extraction of BTX from naphtha reformate using a mixer-settler cascade. *Solv Extract Ion Exchange* **7**: 677–703 (1989).