

Solute recovery from ionic liquids: A conceptual design study for recovery of styrene monomer from [4-mebupy][BF₄]



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ABSTRACT

Extractive distillation using ionic liquids (ILs) is a promising technology to separate the close-boiling mixture ethylbenzene/styrene. A proper solvent regeneration is crucial to obtain a technical and economic feasible process. In this work, several regeneration technologies were studied to recover styrene from the IL [4-mebupy][BF₄] using Aspen Plus. Stripping with a hot gas (N₂ or ethylbenzene), supercritical CO₂ extraction, distillation by adding a co-solvent, and evaporation were investigated. It was found that the IL that was fed as solvent to the extractive distillation column should have a purity of at least 99.6 wt% to maintain the purities of the top and bottom products from the extractive distillation column. This purity could not be obtained with an evaporator using mild conditions ($T = 130\text{ }^{\circ}\text{C}$, $T_{\text{condenser}} \geq 20\text{ }^{\circ}\text{C}$). From the process models and the economic evaluation for a typical production capacity of 500,000 mta, the conclusion can be drawn that evaporation using very low pressures ($P < 10\text{ mbar}$) and stripping with ethylbenzene are the most promising technologies to recover styrene monomer from the IL [4-mebupy][BF₄].

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1. Introduction

The close-boiling mixture ethylbenzene/styrene is currently industrially separated by distillation [1]. Due to the low relative volatility of the ethylbenzene/styrene mixture, this distillation requires a large reflux of 7.1 and 70 equilibrium stages [1]. A typical production capacity of a styrene production plant is 500,000 metric tonnes annually (mta). Extractive distillation is a promising technology to reduce the capital and operational expenditures (CAPEX and OPEX) to separate close-boiling mixtures [2]. A commonly applied organic solvent in extractive distillation processes is sulfolane [3], which can increase the relative volatility of the ethylbenzene/styrene mixture up to 2.3 [2,4]. A promising alternative to traditional organic solvents are ionic liquids (ILs), which can decrease the OPEX and CAPEX to an even larger extent [5].

Abbreviations: CAPEX, capital expenditures; DIPPR, Design Institute for Physical Property Data; EB, ethylbenzene; IL, ionic liquid; LLE, liquid–liquid equilibrium; [4-mebupy][BF₄], 4-methyl-*N*-butylpyridinium tetrafluoroborate; mta, metric tonnes annually; MESH, material equilibrium summation heat; NMP, *N*-methyl-2-pyrrolidinone; NRTL, non-random two liquid; NTS, number of theoretical stages; OPEX, operational expenditures; ppm, parts per million; ScCO₂, supercritical carbon dioxide; SM, styrene monomer; SF, sulfolane; TAC, total annual costs; VLE, vapor–liquid equilibrium.

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An IL integrates the advantages of a liquid solvent (easy operation) and a solid salt (high separation ability) and is reported as a “green solvent”, because of its negligible vapor pressure [6,7]. The other reported advantageous properties of ILs over commonly applied organic solvents are their designer solvent properties by changing the cation–anion combination [8,9], high chemical and thermal stability [8], broad liquid range [10], and the high capacity of ILs for aromatic components [11]. Moreover, in our ionic liquid screening study we have demonstrated that many ILs have a larger selectivity than sulfolane for separating the ethylbenzene/styrene mixture [12]. Consequently, a lower reflux ratio can be used in the extractive distillation column using ILs. A process design should indicate whether the extractive distillation processes are beneficial compared to the current distillation process from OPEX and CAPEX perspective and whether ILs can outperform sulfolane.

A proper solvent regeneration is crucial to obtain a technically and economically feasible extractive distillation process [3,5]. For the extractive distillation process with sulfolane, a distillation column is used for the solvent regeneration [2]. Because ILs have a negligible vapor pressure, other regeneration technologies can be applied, e.g. a simple evaporation [5,13,14]. However, although often mentioned as an advantage, the negligible vapor pressure of the ILs might also be a disadvantage, because relatively extreme conditions in terms of temperature and pressure are required in an evaporator to obtain high IL purities. High temperatures are undesired, because styrene tends to polymerize at elevated

Nomenclature

| | |
|-------|--------------------------|
| D | solvent capacity |
| F | feed (kg) |
| M_w | molecular weight (g/mol) |
| P | pressure (Pa) |
| Q | heat (MW) |
| R | reflux ratio |
| S | solvent (kg) |
| T | temperature (K) |
| x | mole fraction |
| w | weight fraction |

Greek symbol

| | |
|----------|---------------------|
| α | relative volatility |
|----------|---------------------|

Subscript

| | |
|-----|----------|
| REB | reboiler |
|-----|----------|

temperatures. A restriction in temperature for styrene of 130 °C is often used as a standard [1]. Therefore, there is a need to investigate alternative regeneration technologies to use in combination with evaporation or as a single regeneration technology.

Reported alternatives are stripping with a hot gas, like nitrogen (N_2) [5] or the top product from the extractive distillation column [15], and supercritical carbon dioxide ($scCO_2$) extraction [16–18]. These three recovery options are typically used in combination with an evaporator and have the advantage that usually no extreme conditions are required [5]. A characteristic of a stripping process with N_2 is that commonly low temperatures ($T < 0^\circ C$) are required to condense the stripped product from N_2 [19]. This means that refrigerant has to be used as a coolant, which can increase the OPEX and CAPEX significantly. This drawback can be overcome by applying the top product from the extractive distillation column as a stripping gas. A possible disadvantage of this option is the reduction of process flexibility due to the introduction of several extra streams/refluxes that connect the different unit operations. $scCO_2$ extraction of a solute from the IL has the advantage that CO_2 is a “green solvent” as well [16,17], and has already proven to be a viable solvent in coffee decaffeination and dry cleaning industries [16]. The main drawbacks of $scCO_2$ extraction are the large OPEX to pressurize the CO_2 to supercritical conditions [20], and that the recovery of styrene from CO_2 might also require low temperatures ($T < 0^\circ C$).

Distillation is another option to recover organics from ILs by the addition of a low volatile organic co-solvent to the IL. Thereby, the extreme conditions in the styrene recovery from the IL could be avoided due to the small vapor pressure of the co-solvent. The co-solvent/IL blend will be recycled to the extractive distillation column, where the bottleneck of applying this recovery technology lays. The organic co-solvent will lower the selectivity of the IL for the ethylbenzene/styrene mixture and some extra stages should be added to the top of the column to avoid contamination of the top product. In this study, sulfolane and *N*-methylpyrrolidinone (NMP) have been selected as co-solvents, because sulfolane and NMP increase the relative volatility of the ethylbenzene/styrene mixture up to 2.3 [4] and 1.8–2 [21], respectively. Therefore, both co-solvents do not strongly influence the selectivity of the IL for the ethylbenzene/styrene mixture.

The objective of the work described in this manuscript is to investigate several options to regenerate styrene monomer from the IL 4-methyl-*N*-butylpyridinium tetrafluoroborate ([4-mebupy][BF_4]). This IL was selected based on the results of an extensive experimental solvent screening study [12].

[4-mebupy][BF_4] can increase the relative volatility of the EB/SM mixture up to 2.8, which is higher than the benchmark solvent sulfolane [27]. Moreover, [4-mebupy][BF_4] has a relatively high solvent capacity for both aromatics ($w_{max} = 0.234$ for ethylbenzene; $w_{max} = 0.414$ for styrene [27]). In this study, first the operational settings of the extractive distillation column were determined by a sensitivity analysis. Next, the effect of different styrene concentrations in the IL recycle was examined on the required reflux ratio and reboiler heat duty of the extractive distillation column. The results from this sensitivity analysis were required to find the minimum required purity of the IL recycle. Subsequently, it was investigated which purity can be obtained by an evaporator using mild conditions ($T < 130^\circ C$, $T_{condenser} \geq 20^\circ C$), after which the other regeneration technologies were modelled. Finally, an analysis was made of the OPEX and CAPEX, and total annual costs (TAC) to determine the most promising regeneration technology to recover styrene from the IL [4-mebupy][BF_4].

2. Process descriptions regeneration technologies

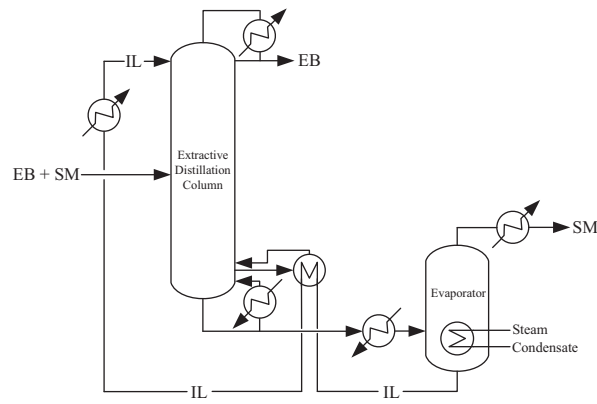
In this section, the final process schemes and their descriptions of the different regeneration technologies in combination with the extractive distillation column are provided. The process schemes of the regeneration processes are illustrated in Fig. 1.

2.1. Evaporation under mild conditions

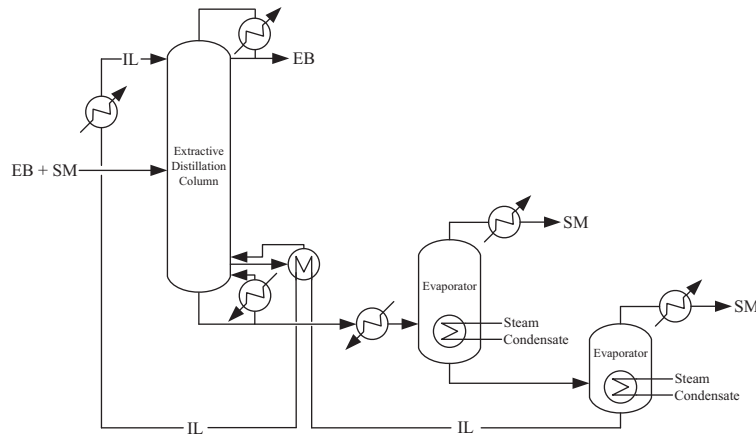
The process scheme with one evaporator as a regeneration technology is depicted in Fig. 1a. This process scheme is the preferred option, because evaporation is the least complicated technology to recover styrene from [4-mebupy][BF_4]. The ethylbenzene/styrene feed and the solvent [4-mebupy][BF_4] are fed to the middle and the top of the extractive distillation column, correspondingly. [4-mebupy][BF_4] can be fed completely at the top of the extractive distillation column, because ILs do not have a significant vapor pressure and therefore will not contaminate the top product. Ethylbenzene leaves the extractive distillation column at the top, because it has a higher vapor pressure than styrene and [4-mebupy][BF_4] is more selective towards styrene. Styrene and [4-mebupy][BF_4] leave the column at the bottom and are fed to the evaporator, where the styrene is evaporated from [4-mebupy][BF_4]. The bottom stream from the extractive distillation column is fed first to a heat exchanger, which heats this stream to the temperature of the evaporator. The evaporator depicted in Fig. 1a operates at mild conditions, which means a temperature not higher than 130 °C [1] and vacuum pressures at which still normal cooling water of 20 °C can be used to condense the evaporated styrene. The IL from the evaporator is recycled back to the top of the extractive distillation column. The IL from the evaporator contains a large amount of heat and requires a cool down from 130 °C to the temperature of the top of the extractive distillation column. Therefore, heat integration was performed by adding an extra reboiler at the bottom of the extractive distillation column. This reboiler is driven by the heat released by the IL and thereby minimizes the heat requirement for solvent heating. This type of heat integration is common practice in extractive distillation processes [2]. One extra heat exchanger was required to cool down the IL recycle to the temperature of the top of the extractive distillation column.

2.2. Evaporation at very low pressures

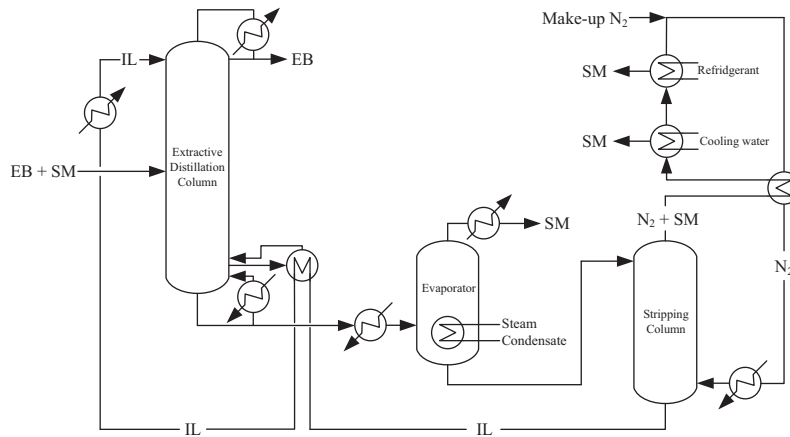
The process scheme for evaporation at very low pressures (<10 mbar) is illustrated in Fig. 1b. The flow sheet is similar to the one shown in Fig. 1a, except that an extra evaporator is added after the first evaporator. If the first evaporator that operates at mild conditions cannot meet the purity requirements of the IL recycle,



a. Process scheme for extractive distillation process with an evaporator.

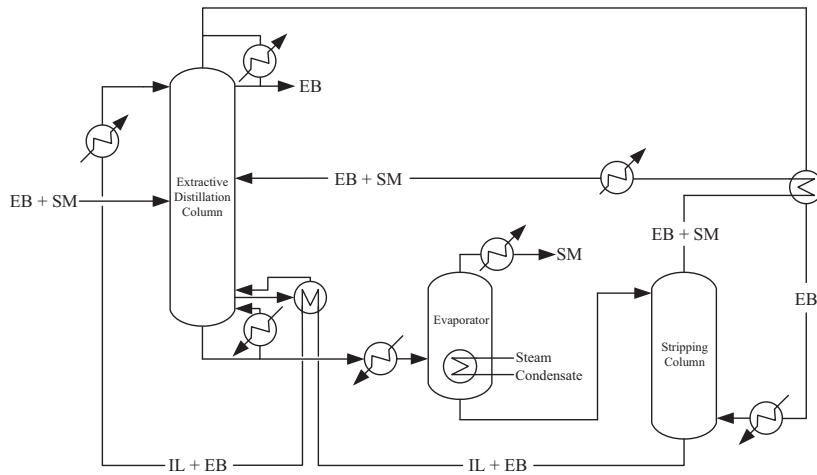


b. Process scheme for extractive distillation process with two evaporators as regeneration technology. The first evaporator is operating at mild conditions ($T = 130\text{ }^{\circ}\text{C}$, $T_{\text{condenser}} \geq 20\text{ }^{\circ}\text{C}$), the second evaporator at very low pressures.

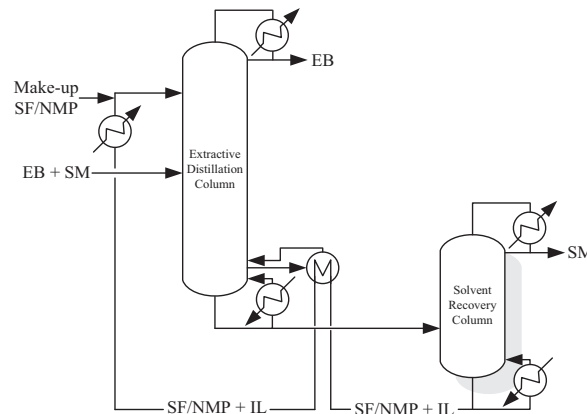


c. Process scheme for extractive distillation process with nitrogen stripping.

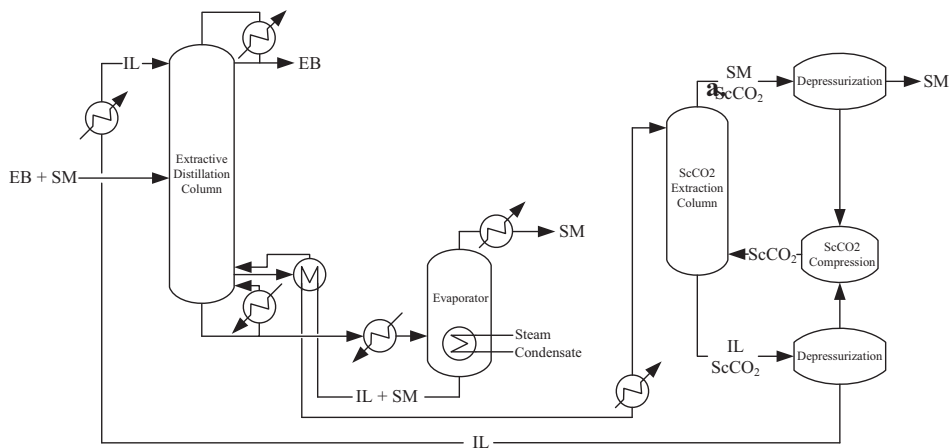
Fig. 1. Process schemes for the different regeneration technologies [a, evaporator; b, two evaporators as regeneration technology. The first evaporator is operating at mild conditions ($T = 130\text{ }^{\circ}\text{C}$, $T_{\text{condenser}} \geq 20\text{ }^{\circ}\text{C}$), the second evaporator at very low pressures; c, nitrogen stripping; d, ethylbenzene stripping; e, distillation; f, super critical carbon dioxide extraction] in combination with the extractive distillation column. EB, ethylbenzene; SM, styrene; IL, [4-mebupy][BF₄]; SF, sulfolane; NMP, *N*-methylpyrrolidinone; N₂, nitrogen; scCO₂, supercritical carbon dioxide.



d. Process scheme for extractive distillation process with ethylbenzene stripping.



e. Process scheme for extractive distillation process with distillation.



f. Process scheme for extractive distillation process with super critical carbon dioxide extraction.

Fig. 1. (continued).

an extra purification step is required. To increase the purity of the IL recycle, the second evaporator has to operate at lower pressures than the first evaporator, because the maximum operating temperature must not exceed 130 °C. Chilled cooling water ($\approx 7^\circ\text{C}$) or refrigerant is required to condense the evaporated styrene from the second evaporator. It was also investigated whether it would be more beneficial to compress the vapor stream from the second

evaporator to higher pressure to be able to apply normal cooling water.

2.3. N₂ stripping

The schematic view of the N₂ stripping process is shown in Fig. 1c. In this process, an evaporator that operates at mild

conditions is used as well to recover first a large part of the styrene from the IL in order to reduce the N_2 flow. The final polishing of the IL to higher purities is performed in the N_2 stripping column. The stream from the evaporator is fed to the top of the stripping column and the N_2 is fed countercurrently from the bottom. The purified IL leaves the stripping column at the bottom and is recycled to the extractive distillation column. The stripped styrene and N_2 leave the stripper at the top. First, the stream is lead through a heat exchanger where heat is exchanged with the cold N_2 that is recycled to the stripping column. After the heat exchanger, the stream is fed through two condensers to recover the styrene product. The first and second condenser use normal cooling water of 20 °C and refrigerant, respectively. The purified N_2 is recycled to the bottom of the stripping column.

2.4. Ethylbenzene stripping

The ethylbenzene stripping process is depicted in Fig. 1d. Here, ethylbenzene from the top of the extractive distillation column is used as the stripping agent instead of N_2 . The ethylbenzene stripping gas is heated to the temperature of the stripping column by a heat exchanger and a heater. The ethylbenzene stripping gas is contacted countercurrently with the liquid feed in the stripper. The bottom stream from the stripper, containing [4-mebupy][BF₄] and ethylbenzene, is recycled to the extractive distillation column. The ethylbenzene in the IL recycle does not have a negative impact on the extractive distillation column performance, because ethylbenzene is already introduced to the top of the extractive distillation column via the distillate reflux. The distillate reflux will decrease if ethylbenzene is introduced to the top of the extractive distillation column via the IL recycle. However, the reflux is also dependent on the styrene concentration in the IL recycle, which is presented later on in this paper. The top stream of the ethylbenzene stripper consists of styrene and ethylbenzene. This stream is contacted indirectly in a heat exchanger with the ethylbenzene stripping gas from the top of the extractive distillation column. Subsequently, the ethylbenzene/styrene stream is liquefied using a condenser and fed to the extractive distillation column.

2.5. Distillation with the blends NMP/IL and sulfolane/IL

The recovery process through distillation is illustrated in Fig. 1e, in which the blends NMP/IL and sulfolane/IL are used as the solvents. In this process, the blend mixture is introduced a few stages below the top to avoid contamination of the top product of the extractive distillation column, because contrary to the IL, the vapor pressure of NMP and sulfolane is not negligible. The bottom stream from the extractive distillation column is fed to the solvent recovery column, where styrene is obtained at the top. The solvent blend leaves the recovery column at the bottom and is recycled to the extractive distillation column. A make-up stream of the organic co-solvents is added to the solvent recycle stream to account for the small solvent losses of sulfolane/NMP at the tops of both distillation columns.

2.6. Supercritical carbon dioxide extraction

The process with $scCO_2$ extraction as recovery technology is shown in Fig. 1f. Similar to the processes that make use of stripping as recovery technology (Fig. 1c and d), here an evaporator is used as well to reduce the amount of $scCO_2$ that is required for the recovery. The bottom stream of the evaporator in this process is fed to the $scCO_2$ extraction column, which operates at much lower temperatures, preferably at 40 °C [16]. Therefore, heat integration is performed first with the extractive distillation column before feeding it to the $scCO_2$ extraction column. The IL/styrene

mixture from the evaporator and the $scCO_2$ stream are fed to the extraction column countercurrently. In this column, the styrene is transferred from the IL phase to the $scCO_2$. The IL does not dissolve in the $scCO_2$, because it does not have a vapor pressure [16]. The styrene and $scCO_2$ leave the extraction column at the top and after depressurization of this stream, pure styrene is obtained. Possibly, a condenser is required to obtain the styrene after depressurization, depending on the amount of $scCO_2$ required to extract the styrene from [4-mebupy][BF₄]. Some $scCO_2$ will leave the extraction column via the bottom, because CO_2 has a significant solubility in ILs [22]. After depressurization of this stream, pure IL and CO_2 are obtained. The CO_2 streams from both depressurization units are fed to a compression unit, which compresses the CO_2 back to supercritical conditions.

3. Process modelling and calculation of operational and capital expenditures

The model choice, simulation package, modelling approach, model input, operating conditions and the input for the calculation of the OPEX and CAPEX are discussed in this section. The required parameters for the physical property models used in this study have been reported recently [4,12,27,32].

3.1. Equilibrium stage model

An equilibrium stage model was used to model the extractive distillation column and the regeneration technologies, except for the $scCO_2$ extraction regeneration technology. An equilibrium stage model assumes physical equilibrium between the vapor and liquid phases [23], which is sufficient for a first evaluation of the various regeneration technologies. The equilibrium stage model is based on the MESH (Material, Equilibrium, Summation, and Heat balance) equations and was simulated in Aspen Plus. The inside-out RadFrac model was used in combination with Newton's algorithm to model the extractive distillation column. The Newton's algorithm is recommended for highly non-ideal systems and is better for columns with highly sensitive specifications [24,25]. The N_2 and ethylbenzene stripping columns were modelled with the RadFrac model as well. The evaporators were modelled with a two-outlet Flash vessel.

3.2. Thermodynamics

The modified Raoult's law was used to describe the physical equilibrium between the vapor and liquid phase [23]. The vapor phase was assumed to be ideal, because all processes were modelled from deep vacuum to atmospheric pressure [23]. Moreover, the vapor phase consisted mainly of ethylbenzene and styrene, which are components with similar molecular structures. The Antoine equation was used to calculate the pure component vapor pressures of ethylbenzene, styrene, sulfolane, and NMP. The Antoine parameters for ethylbenzene [4], styrene [4], and sulfolane [26] were taken from previous work and for NMP from the Aspen Plus database. A vapor pressure of zero was attributed to the IL [4-mebupy][BF₄], because ILs have a negligible vapor pressure. The NRTL model was used to calculate the activity coefficients of the components in the liquid phase. The NRTL model was selected, because it can describe vapor–liquid equilibrium (VLE) as well as liquid–liquid equilibrium (LLE) for multicomponent systems [23]. The binary NRTL parameters between all components have to be known to get a proper description of the non-ideal behaviour in the liquid phase [23]. The NRTL parameters between the IL [4-mebupy][BF₄] and ethylbenzene/styrene were required for the processes with evaporation, N_2 stripping, and ethylbenzene stripping as regeneration technologies. These NRTL parameters have been determined in previous work [27]. For systems containing ILs,

Table 1

The binary NRTL parameters for the systems (ethylbenzene + styrene + *N*-methylpyrrolidinone), (*N*-methylpyrrolidinone + [4-mebupy][BF₄]), and (sulfolane + [4-mebupy][BF₄]).

| Component <i>i</i> Component <i>j</i> | Ethylbenzene <i>N</i> -Methylpyrrolidinone | Styrene <i>N</i> -Methylpyrrolidinone | <i>N</i> -Methylpyrrolidinone [4-mebupy][BF ₄] | Sulfolane [4-mebupy][BF ₄] |
|--|---|--|---|---|
| a_{ij} | 0 | 0 | 0 | 0 |
| a_{ji} | 0 | 0 | 0 | 0 |
| b_{ij} | 350.04 | 327.34 | 257.55 | 298.65 |
| b_{ji} | -65.58 | -192.59 | -287.49 | -339.78 |
| α_{ij} | 0.3 | 0.3 | 0.3 | 0.3 |

it is difficult to describe binary and ternary VLE data with a single set of binary NRTL parameters [27,28]. Therefore, the NRTL parameters regressed solely from the ternary VLE data and binary LLE data were used to model the extractive distillation column and the ethylbenzene stripper and the parameters from merely the binary VLE data and binary LLE data were applied to model the other recovery technologies. To model the distillation recovery technology, in which NMP and sulfolane were used as co-solvents, the binary NRTL parameters have to be known between sulfolane (or NMP) and the components ethylbenzene/styrene/[4-mebupy][BF₄]. The parameters for the ternary system ethylbenzene/styrene/sulfolane have been determined previously [4]. The NRTL parameters between ethylbenzene/styrene and NMP were determined by the group contribution method UNIFAC [29] using the Dortmund Databank parameters in Aspen Plus, because the NRTL parameters for this system are not available in the open literature. The obtained NRTL parameters for this system are listed in Table 1. The other required NRTL parameters between sulfolane/[4-mebupy][BF₄] and NMP/[4-mebupy][BF₄] were determined from activity coefficients at infinite dilution [23] and are also listed in Table 1. The activity coefficients at infinite dilution were determined by the software package COSMO-RS at 100 °C [30,31].

The liquid heat capacity is another important property to model the extractive distillation processes. The DIPPR (Design Institute for Physical Property Data) equation was used to calculate the specific liquid heat capacity of the different components. The parameters to calculate the specific heat capacity for ethylbenzene, styrene, NMP, and sulfolane were taken from the Aspen Plus databank. The DIPPR parameters for [4-mebupy][BF₄] were taken from Bandres and co-workers [32].

3.3. Model Input

3.3.1. Feed conditions and purity requirements

The ethylbenzene/styrene feed to the extractive distillation column was 100 metric tonnes/hr, with a styrene concentration of 60 mol% [1]. The feed entered the column at its boiling point. The required ethylbenzene purity at the top of the extractive distillation column was 98.3 mol% [1]. The ethylbenzene impurity level in the final styrene product was set to 100 ppm. The top and bottom flows were calculated by a mass balance. The temperature of the IL was set to its feed tray temperature.

3.3.2. Extractive distillation column

The condenser pressure was set to 50 mbar to keep low temperatures in the extractive distillation column, and thereby minimizing the amount of styrene polymerization. The structured packing Mellapak 250X is often applied for ethylbenzene/styrene splitters due to its low pressure drop [1,33] and was chosen as internal. A thermosyphon reboiler was used in the model, which is often applied to distill thermally sensitive components [1,34]. The IL was fed to the top stage of the extractive distillation column. The ethylbenzene/styrene feed entered the column at the stage where the ethylbenzene/styrene ratio was similar the ethylbenzene/styrene feed ratio. A sensitivity analysis was performed to

obtain the operational settings of the extractive distillation column. The following parameters were varied: solvent-to-feed (*S/F*) ratio, number of equilibrium stages (NTS), and reflux ratio. These three parameters have the largest influence on the performance of an extractive distillation column [3,35]. First, the minimum required *S/F* ratio was determined to avoid multiple liquid phases in the extractive distillation column, because [4-mebupy][BF₄] is not fully miscible with ethylbenzene and styrene [12]. Multiple liquid phases in an extractive distillation process should be avoided, because it decreases the process efficiency [35,36]. Subsequently, the *S/F* ratio was varied up to 7 on mass base, and the number of theoretical stages was varied from 35 to 60 with a step change of 5. The reflux ratio was calculated by a design specification in Aspen Plus, in which the required ethylbenzene impurity level of 100 ppm in the styrene bottoms product was set as the target. The regeneration technologies were modelled all together with the extractive distillation column. The recycling streams from the regeneration technologies differ in composition and therefore have different effects on the extractive distillation performance.

3.3.3. Purity requirement IL recycle

The effect of the styrene concentration in the IL recycle on the extractive distillation column performance was investigated to determine up to which purity the IL needs to be purified. The styrene concentration in the IL recycle was varied from 0 to 0.5 wt%. The reflux ratio was varied by a design specification in Aspen Plus to meet the purity requirements of the top and bottom products.

3.3.4. Evaporation

First, the minimum vacuum pressure in the evaporator was determined to still be able to condense the evaporated styrene with normal cooling water of 20 °C. A temperature difference of 10 °C over the condenser was used [19], meaning that the minimum allowable vacuum pressure was determined at 30 °C. Next, the pressure and temperature of the evaporator were varied to determine the IL purity, which can be obtained at mild conditions.

3.3.5. Evaporation at very low pressure

Very low pressures are required if the IL purity specification cannot be obtained using an evaporator at mild conditions. The required pressures were determined for several purities of the IL recycle using a design specification in Aspen Plus. These IL purities were determined by a design specification, because it was expected that a higher IL purity would require more heating/cooling in the regeneration section, but would have a beneficial effect on the extractive distillation column performance.

3.3.6. N₂ stripping

The N₂ stripping column was modelled at a pressure of 1 atm and a temperature of 130 °C. The NTS and N₂ flow are the two parameters, which have the largest influence on a stripping process [37]. The NTS were varied and via a design specification the required N₂ flow was determined for several IL purities. Subsequently, the total stripping process was modelled including the extractive distillation column for several IL recycle purities.

3.3.7. Ethylbenzene stripping

The ethylbenzene stripping column was simulated at a temperature of 130 °C as well. The pressure in the ethylbenzene stripping column was varied from 16.8 to 40 mbar. 16.8 mbar was determined as the minimum allowable vacuum pressure for the stripping column, because at this pressure ethylbenzene can still be condensed using normal cooling water of 20 °C. A pressure of 40 mbar was used as the highest pressure, because this avoids the need for a compressor to transport the ethylbenzene from the extractive distillation, which operates at 50 mbar, to the ethylbenzene stripping column. The required ethylbenzene flow was determined in the same manner as for N₂ stripping and finally the total process was modelled including the extractive distillation column.

3.3.8. Distillation with NMP/IL and sulfolane/IL blend

First, the effect of several NMP/IL and sulfolane/IL mass ratios on the relative volatility of the ethylbenzene/styrene mixture was determined. This effect was determined by a Flash vessel in Aspen Plus at 50 mbar. The *S/F* ratio determined by the sensitivity analysis for the extractive distillation column was applied. The ethylbenzene/styrene mass ratio was 40/60. Based on these results, the NMP/IL and sulfolane/IL ratios were selected and used as input for the model of the extractive distillation column. Next, the amount of stages which needed to be added to the top of the extractive distillation column was determined to avoid contamination of the ethylbenzene top product ($w_{SF/NMP} < 1$ ppm). Subsequently, the NTS for the regeneration column was determined, which was followed by the model of the total process. The purity of the blend to be recycled to the extractive distillation column was set to 99.9 wt% (i.e. 0.1 wt% styrene). The regeneration columns were both modelled at 11.1 mbar, to keep the temperatures in the reboiler as low as possible. The NTS were varied to determine the required reflux ratio.

3.3.9. scCO₂ extraction

The regeneration process using scCO₂ extraction was not modelled in Aspen Plus, because there were no interaction parameters available for this system in the open literature or in the Aspen Plus database. Moreover, Aspen Plus has difficulties to calculate the power required to compress CO₂ to supercritical conditions properly [38]. Therefore, a process design was made using literature data by Blanchard and co-workers [16] about the recovery of organic products, like benzene, from the IL 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF₆]) using scCO₂ extraction. The systems studied by Blanchard et al. are similar to the system studied in this work. Benzene and styrene are both aromatic components having a flat molecular structure [39]. The ILs [BMIM][PF₆] and [4-mebupy][BF₄] both have an aromatic cation containing a butyl and a methyl group as side chains. Moreover, both of them have a spherical anion. Therefore, a first estimate can be made about the OPEX using the LLE data of Blanchard et al. In their manuscript, the organic product recovery percentage as function of the scCO₂/organic product ratio is reported. From the LLE data for the system (benzene + [BMIM][PF₆] + scCO₂), the solvent capacity was calculated using a mass balance over the extraction experiment. With the solvent capacity, the minimum required solvent flow for our system could be calculated. The required solvent flow was corrected by the molecular weight difference between styrene ($M_w = 104.2$ g/mol) and benzene ($M_w = 78.1$ g/mol). The CO₂ solubility in [4-mebupy][BF₄] was also taken into account using another article published by Blanchard et al. [22]. Finally, the energy requirements for the CO₂ compression system were calculated from the total scCO₂ flow using data from Maramba and Bhatlacharya [40].

Table 2

Cost factors for the operational expenditures [19,41].

| Cost factor | €/GJ |
|--------------------------------|------|
| <i>Heating</i> | |
| Steam medium pressure (10 bar) | 9.95 |
| Steam low pressure (3.4 bar) | 6.22 |
| <i>Cooling</i> | |
| Cooling water (>32 °C) | 0.80 |
| Cooling water (20 °C) | 1.73 |
| Chilled water (7 °C) | 12.3 |
| Ammonia (−34 °C) | 24.7 |

3.4. Operational and capital expenditures

The OPEX and CAPEX were calculated to make a proper comparison between the regeneration processes. The OPEX were calculated from the heating and cooling duties provided by the Aspen Plus simulations. The used cost factors to calculate the OPEX are shown in Table 2. A running time of 8400 h per year was used to calculate the OPEX per year [41].

Aspen Process Economic Analyzer was used to determine the CAPEX of the different regeneration processes. The dimensions of all (extractive) distillation columns were calculated directly in Aspen Plus using the Packing Sizing tool and exported to Aspen Process Economic Analyzer [24]. The areas of the thermosyphon reboilers, condensers, and heat exchangers were calculated using standard overall heat transfer coefficients [42]. Shell-and-tube heat exchangers were used for the condensers and heat exchangers. A forced circulation evaporator was selected to determine the CAPEX of the evaporators, because of their proven application for thermally sensitive mixtures [34]. A falling film evaporator was chosen as the second evaporator for the recovery option using extra low vacuum pressures [42]. The purchase costs of pumps were not taken into account. It was also assumed that utilities, like a refrigeration unit e.g., are already available at the plant site. Stainless Steel 316 was selected as the material type, because ILs are known as slightly corrosive fluids [43,44]. The total solvent investment was calculated from the total solvent hold-up in the process and the price per kg. The assumption was made that the price of the IL [4-mebupy][BF₄] is € 25/kg [45]. Sulfolane and NMP cost € 2.78/kg [46] and € 2.07/kg [47], respectively.

4. Results and discussion

In this section, the results are presented for the different regeneration technologies. First, the results of the sensitivity analysis for the extractive distillation column are discussed, followed by the influence of the styrene concentration in the IL recycle on the performance of the extractive distillation column. Subsequently, the results are discussed for the different regeneration technologies. Finally, the results for the OPEX and CAPEX calculations for the different regeneration technologies are presented.

4.1. Extractive distillation column

The sensitivity analysis for the extractive distillation column involved minimization of the reflux ratio as function of the *S/F* ratio and the number of stages. In order to ensure a homogeneous liquid phase over the complete column, the minimum required *S/F* ratio was 3.8 kg IL/kg. Fig. 2a shows that the reflux ratio decreases slightly with increasing *S/F* ratio, which is common for extractive distillation columns [35]. The relative volatility increases with increasing *S/F* ratio, and thereby the reflux ratio can decrease to obtain the same top and bottom purity. Commonly, the minimum reflux ratio is a strong function of the *S/F* ratio, especially at low

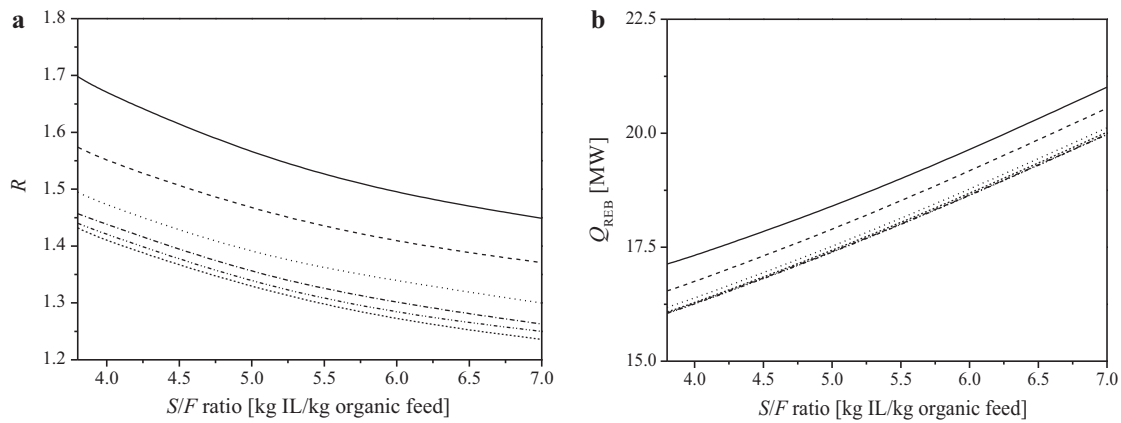


Fig. 2. (a) Reflux ratio (R) as function of S/F ratio and number of stages (NTS). (b) Reboiler heat duty (Q_{REB}) as function of S/F ratio and NTS. (—) NTS = 35; (---) NTS = 40; (···) NTS = 45; (-·-·) NTS = 50; (-··-) NTS = 55; (·-·) NTS = 60.

S/F ratios [4,36]. The effect of increasing S/F ratio becomes smaller at higher S/F ratios [4]. A rather large S/F ratio (i.e. a large molar IL/organic ratio on the equilibrium trays) is a prerequisite to obtain a homogeneous liquid phase, and therefore the reflux ratio is not strongly decreasing with increasing S/F ratio for the system studied here. Fig. 2b displays the reboiler heat duty, which increases with increasing S/F ratio. The supplied energy to the reboiler is mainly used to obtain a certain boil up (evaporation) rate in the extractive distillation column and to heat up the solvent [35]. The energy required for evaporation decreases only slightly with increasing S/F ratio. However, the amount required for solvent heating increases linearly with increasing S/F ratio. Therefore, an S/F ratio of 3.8 was selected to keep the energy requirements for heating up the solvent as low as possible. At this S/F ratio, 31% of the energy supplied to the reboiler is required for solvent heating. Fig. 2 also illustrates the influence of the NTS on the reflux ratio and reboiler heat duty, which both decrease with increasing NTS. From Fig. 2b can be seen that at a certain NTS, the reboiler heat duty decreases not significantly with increasing NTS, because the minimum required reflux ratio is approached to obtain the bottom and top purity. 45 NTS were selected, because an increase of the NTS from 45 to 50 resulted in a reboiler heat duty reduction of less than 1% compared, which was used as the criterion to select the NTS. At these settings, the reflux ratio to obtain the top and bottom purity requirements is 1.49. The IL leaving the column at the bottom of the extractive distillation column contains 13.4 wt% styrene and has a temperature of 78.5 °C. These were the input conditions for the different recovery technologies.

4.2. Purity requirement IL recycle

Fig. 3 shows the influence of the styrene concentration in the IL recycle on the reflux ratio (left y-axis) and reboiler heat duty (right y-axis). From this figure the conclusion can be drawn that the reflux ratio and reboiler heat duty both increase with increasing styrene concentration in the IL recycle. The increase of the reboiler heat duty is a direct result from the increase in reflux ratio. A part of the added styrene at the top of the extractive distillation will evaporate at the top stage. Therefore, the reflux ratio must increase to maintain the same ethylbenzene purity ($x_{EB} = 98.3$ mol%). From this analysis, the conclusion can also be drawn that a styrene concentration larger than 0.4 wt% in the IL recycle should be avoided. A larger reflux ratio is required if more styrene is added to the column, and thereby, the IL/organic ratio decreases on the equilibrium trays. This is undesirable, because it causes liquid–liquid phase splitting at a styrene concentration larger than 0.4 wt%. A larger S/F ratio can be applied to maintain a homogeneous liquid phase. However, more

styrene will be added to the extractive distillation column via the IL recycle, if a larger S/F ratio is applied. Therefore, a larger reflux ratio is required to maintain the ethylbenzene purity at the top of the column, by which the IL/organic ratio decreases, etc. It is not possible to get out of this loop. The maximum styrene concentration in the IL recycle is thus 0.4 wt%, meaning a minimum IL purity of 99.6 wt%. This criterion was used to explore if the regeneration technologies can meet this purity specification, which is explained in the next section. However, higher IL purities (>99.6 wt%) are preferred, because it clearly gives a lower reboiler heat duty.

4.3. Evaporation

The proposed process scheme using a single evaporator as the regeneration technology is shown in Fig. 1a. The pure component vapor pressure curve of styrene is depicted in Fig. 4a. The dotted line in Fig. 4a indicates the pressure at which normal cooling water of 20 °C can be applied to condense the styrene vapor from the evaporator. From this analysis, the conclusion can be drawn that a minimum vacuum pressure of 11.1 mbar can be applied. In Fig. 4b the obtained IL mass fraction is shown as a function of temperature and pressure using an evaporator. The IL mass fraction increases with increasing temperature and decreasing pressure. This relation can be derived from the modified Raoult's law. The straight short dotted line in Fig. 4b illustrates the minimum required purity for the IL recycle. A maximum temperature of 130 °C was selected for the recovery technologies to keep the formation of styrene polymer low. An IL recycle purity of 99.5 wt% was obtained at this

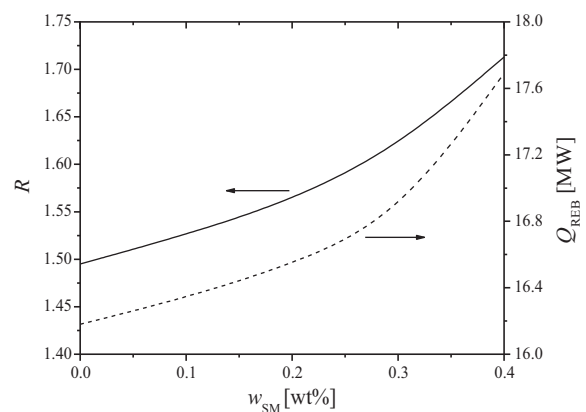


Fig. 3. Influence of styrene mass concentration (w_{SM}) in the ionic liquid recycle on the reflux ratio (R) and reboiler heat duty (Q_{REB}) of the extractive distillation. (—) R ; (---) Q_{REB} .

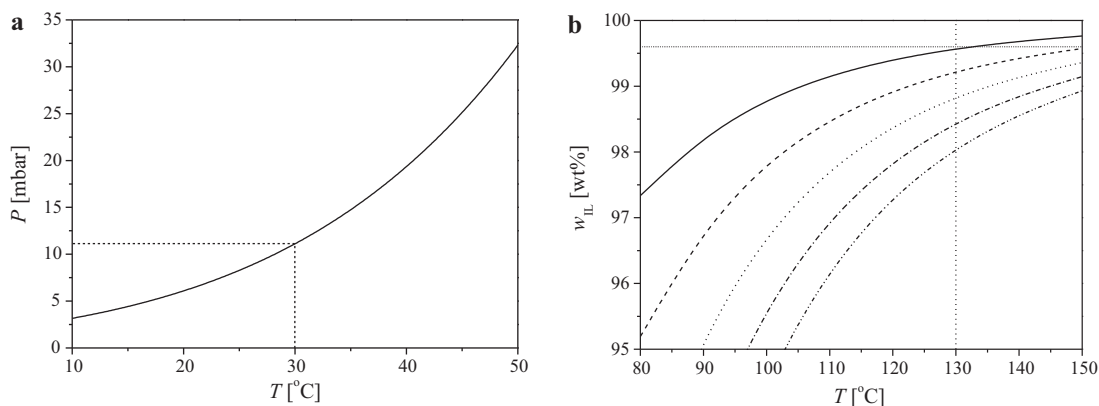


Fig. 4. (a) Pure component vapor pressure of styrene. The dotted line indicates the styrene pressure at which normal cooling water of 20 °C could be used to condensate styrene, assuming a ΔT of 10 K over the heat exchanger. (b) Ionic liquid purity (w_{IL}), which can be obtained by evaporation as function of pressure (P) and temperature (T). The straight short dotted line is the minimum required IL purity by evaporation at mild conditions. (—) $P=11.1$ mbar; (---) $P=20$ mbar; (···) $P=30$ mbar; (-·-) $P=40$ mbar; (-·-·) $P=50$ mbar.

temperature and the minimum pressure of 11.1 mbar, which corresponds to a styrene recovery of 97%. The use of an evaporator using these conditions is thus not sufficient to obtain the minimum required IL recycle purity. Therefore, many other regeneration technologies were explored, which are discussed in the following sections. The other regeneration technologies were all, except for the regeneration using distillation, investigated in combination with the evaporator, which operates at 130 °C and 11.1 mbar. This evaporator thus recovers a major part (97%) of the styrene from [4-mebupy][BF₄] and thereby minimizes the energy requirements for the other regeneration technologies to polish the IL purity. The polishing technologies were modelled for the IL purities of 99.9, 99.8, and 99.7 wt%, because higher IL purities will give lower reboiler heat duties in the extractive distillation column as explained in Section 4.2. The reboiler heat duty especially increases strongly at IL purities below 99.7 wt%.

4.4. Evaporation at very low pressures

The schematic view on the regeneration process using one evaporator at mild conditions ($T=130$ °C, $P=11.1$ mbar) and one extra evaporator operating at lower vacuum pressures is provided in Fig. 1b. In Fig. 5a the required vacuum pressures (left y-axis) and condenser temperatures (right y-axis) are depicted as function of the IL recycle purity. The required pressure decreases with increasing IL purity. Thereby, the required condenser temperature also decreases, which can be derived from the Antoine equation [23].

The total process, as depicted in Fig. 1b, was modelled for the IL recycle purities: 99.7, 99.8, and 99.9 wt% (see Sections 4.1 and 4.3). A higher IL purity will require more heating and cooling requirements in the evaporator at very low pressure, but will have a beneficial effect on reboiler heat duty of the extractive distillation column. The vacuum pressures in the second evaporator to obtain the IL purities of 99.7, 99.8, and 99.9 wt%, are 7.8, 5.2, and 2.6 mbar, respectively. These are much lower than for the evaporator operating at mild conditions. The heat duty and refrigeration requirements for the total extractive distillation process as function of IL recycle purity are depicted in Fig. 5b. This figure shows that the effect of the IL purity in the recycle on the heat duty requirements for the total process is minor in the purity range evaluated. These small differences in heat duty requirements as function of the IL recycle purity can be explained by the fact that a large styrene recovery (97%, see Section 4.3) is already obtained in first evaporator operating at 130 °C and 11.1 mbar. Therefore, the heat duty requirements for purifying the IL to higher concentrations, using an evaporator at very low pressures, contribute to only 0.2–0.5% of the total heat duty requirements, depending on the IL recycle purity. Moreover, the benefits in heat duty requirements for the extractive distillation column of recycling the IL up to higher purities cancel out with the extra energy required for refrigeration. It was not feasible to compress the vapor from the second evaporator to higher pressures to be able to condense this stream using normal cooling water, because the vapor temperature exceeded the temperature limit of 130 °C. Moreover, the investment costs for a compressor

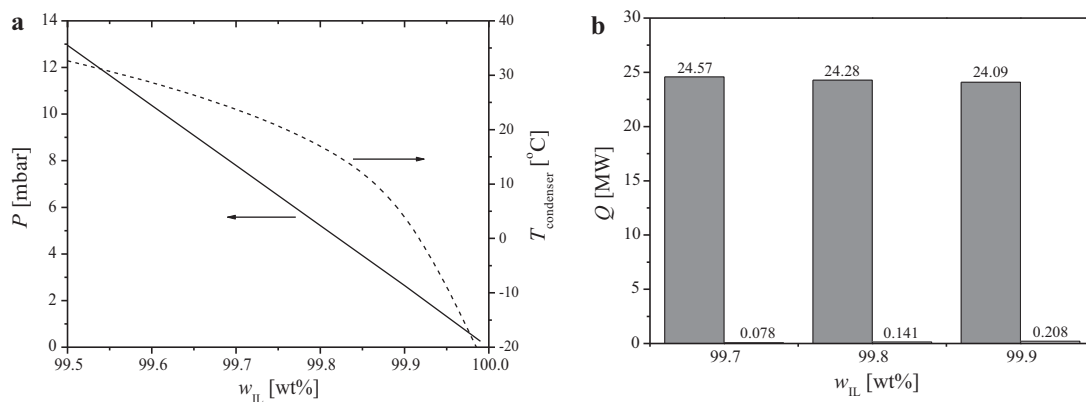


Fig. 5. (a) Required vacuum pressures (P) and condenser temperatures ($T_{condenser}$) to obtain high ionic liquid purities by evaporation at a temperature of 130 °C. (—) Pressure evaporator; (---) required condenser temperature. (b) Heat duty and refrigeration requirements for the total extractive distillation process using two evaporators for different IL recycle purities (w_{IL}). Grey bars, heat duty requirements; light grey bars, refrigeration requirements.

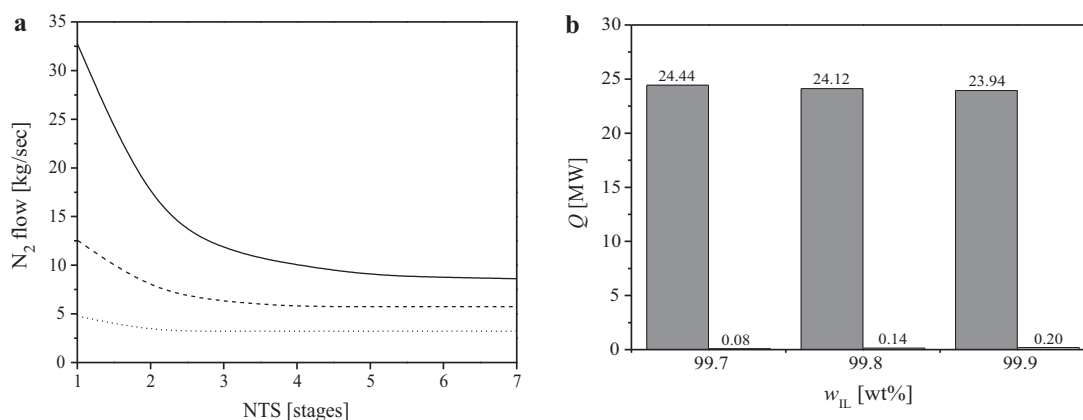


Fig. 6. (a) Required nitrogen (N_2) flow as function of the number of theoretical stages (NTS) to obtain the required IL purity. (—) $w_{IL} = 99.9$ wt%; (---) $w_{IL} = 99.8$ wt%; (⋯), $w_{IL} = 99.7$ wt%. (b) Heat and refrigeration requirements for the total extractive distillation using nitrogen stripping for different IL recycle purities (w_{IL}). Grey bars, heat duty requirements; light grey bars, refrigeration requirements.

were found to be 3–4 times higher than a condenser using refrigerant.

4.5. N_2 stripping

The process with N_2 stripping as the recovery technology is shown in Fig. 1c. Here the evaporator, operating at 130 °C and 11.1 mbar, was used to recover the majority (97%) of the styrene. The bottom stream from this evaporator was fed to the N_2 stripping column. First, the required stripping flow to obtain higher IL purities was determined by varying the NTS of the stripping column. The results for this sensitivity analysis are shown in Fig. 6a for the IL purities of 99.7, 99.8, and 99.9 wt%. Fig. 6a shows that a larger N_2 flow is required to obtain higher IL purities. The N_2 stripping flow clearly decreases with the increasing NTS. The N_2 stripping flow approaches the minimum at infinite NTS. A lower stripping flow leads to lower refrigeration requirements, because it is easier to condense styrene from the N_2 . The selected NTS were 7, 5, and 3 for 99.9, 99.8, and 99.7 wt%, correspondingly. At these NTS, the N_2 stripping flow decreases less than 1–2% compared to using one NTS less, which was used to select the NTS. The total process including the N_2 stripping was modelled for the different IL purities. The heat duties and refrigeration requirements as function of these purities are depicted in Fig. 6b. There are minimal differences in energy requirements for the total process with the different IL recycle purities, which can be explained by the fact that already a large styrene recovery (97%) is obtained in the evaporator. Therefore, heating and refrigeration requirements in the N_2 stripping process are rather low. The N_2 stripping contributes to about 0.1–0.3% of the total heat duty requirements. The benefits in heat duty requirements for the extractive distillation column of recycling the IL up to higher purities cancel out with the extra energy required in the stripping process. The heating requirements for the total process using N_2 stripping as recovery technology (23.9 MW at $w_{IL} = 99.9$ wt%) or evaporation at very low pressures (24.1 MW at $w_{IL} = 99.9$ wt%) are almost similar.

4.6. Ethylbenzene stripping

A schematic view of the process with ethylbenzene stripping is illustrated in Fig. 1d. The bottom stream from the evaporator operating at 130 °C and 11.1 mbar was fed to the ethylbenzene stripping column. For the ethylbenzene stripping process not only the NTS were varied to determine the stripping flow, but different vacuum pressures were applied as well. The pressure of the ethylbenzene stripping column was varied between 16.8 and 40 mbar. The results

from the sensitivity analysis are shown in Fig. 6a, in which the required ethylbenzene stripping flow is depicted as function of NTS and vacuum pressures for an IL recycle purity of 99.8 wt%. The trends for 99.7 and 99.9 wt% were similar. From Fig. 6a it can be seen that the required ethylbenzene stripping flow decreases with decreasing pressure. This behaviour can be explained by the increase in distribution coefficient of styrene between the vapor and liquid phase at decreasing pressures, which can be derived from the modified Raoult's law. Therefore, the required ethylbenzene stripping flow is also much lower compared to the N_2 stripping flow in the N_2 stripping process ($P = 1$ atm). The required ethylbenzene flow decreases with increasing NTS and approaches the minimum required ethylbenzene stripping flow at infinite NTS. The selected NTS were 13, 11, and 7 for the IL purities of 99.9, 99.8, and 99.7 wt%, respectively, which are higher than the N_2 stripping process. This originates from the lower stripping flow in the ethylbenzene stripping process compared to the N_2 stripping process together with the applied criterion to select the NTS (1–2% decrease in stripping flow compared to one stage less). An increase in NTS leads to a lower stripping flow, but since the flow in the ethylbenzene stripping column is already rather low, more stages are required to reach the criterion of 1%. From the sensitivity analysis was also found that the required NTS was hardly dependent on the applied vacuum pressure. The total process was modelled for the different IL recycle purities and different pressures of the ethylbenzene stripping column. The heat duty requirements were calculated from the model results, and are illustrated in Fig. 7b. This figure demonstrates that the heat duty requirements of the total process (24.2–24.6 MW) are hardly dependent on the applied vacuum pressure of the ethylbenzene stripping column and the IL recycle purity. This can also be explained by the fact that 97% of the styrene is already recovered in the evaporator operating at mild conditions. Therefore, the ethylbenzene stripping process does not contribute significantly to the total heat duty requirements (0.5–1%), which was observed for the other recovery processes as well. The heating requirements for the total process are thus also similar compared to the total energy requirements for the processes using N_2 stripping (Section 4.5) or evaporation at very low pressures (Section 4.4).

4.7. Distillation with NMP/IL and sulfolane/IL blend

The process scheme for the extractive distillation process using distillation as the recovery technology is shown in Fig. 1e. The influence of the mass ratio organic solvent/IL on the relative volatility of the ethylbenzene/styrene mixture is depicted in Fig. 8. The relative volatility of the ethylbenzene/styrene mixture decreases with

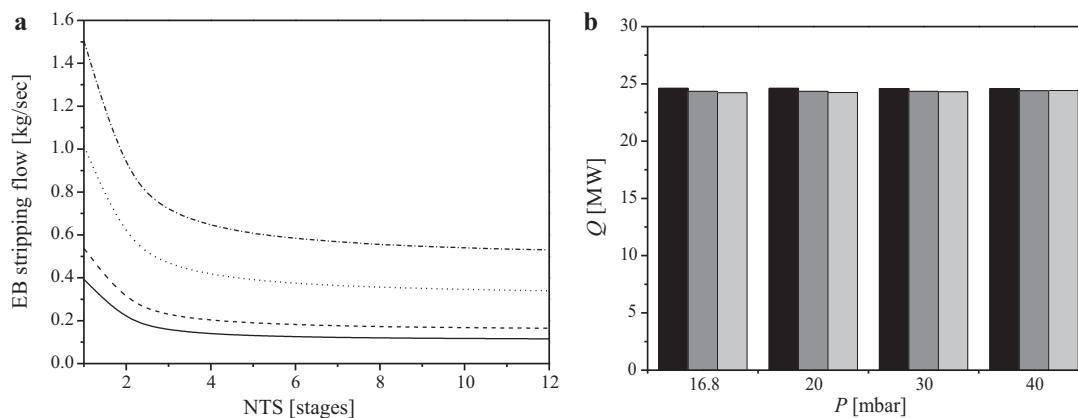


Fig. 7. (a) Required ethylbenzene (EB) stripping flow as function of the number of theoretical equilibrium stages (NTS) for the ionic liquid recycle purity of 99.8 wt%. (—) $P=16.8$ mbar; (---) $P=20$ mbar; (⋯) $P=30$ mbar; (-⋅-) $P=40$ mbar. (b) Heat duty requirements for the extractive distillation process including ethylbenzene stripping for different pressures (P) of the ethylbenzene stripping column and purity of the ionic liquid recycle (w_{IL}). Black bars, $w_{IL}=99.7$ wt%; dark grey bars, $w_{IL}=99.8$ wt%; light grey bars, $w_{IL}=99.9$ wt%.

increasing organic solvent/IL ratio for both co-solvents, which can be explained by the lower selectivity of the organic co-solvents for the ethylbenzene/styrene mixture [12]. NMP has a lower selectivity than sulfolane for the ethylbenzene/styrene mixture, which corresponds to literature data [21]. An organic solvent/IL mass ratio of 0.1 was selected for both organic solvents to be able make a first estimate of the heat duty requirements using distillation as the recovery technology. At this mass ratio, the selectivity is almost similar compared to pure [4-mebupy][BF₄]. First, the feed stages of the solvent blends were determined to keep the solvent concentrations in the ethylbenzene top product below 1 ppm. From the process simulations in Aspen Plus it was found that for sulfolane and NMP 6 and 8 stages, respectively, need to be added to the top of the extractive distillation column. The required reflux ratios of the extractive distillation column using the sulfolane/IL and NMP/IL blends were 1.55 and 1.7, correspondingly, which are both slightly higher compared to using pure [4-mebupy][BF₄] ($R=1.49$). This can be explained by the lower relative volatility of the blends for the ethylbenzene/styrene mixture.

The regeneration column was modelled for an impurity level of the organic solvents in the final styrene product of 1 ppm. The ethylbenzene impurity level was kept at 100 ppm. The results for both blends are illustrated in Fig. 9. The reflux ratio and thereby the

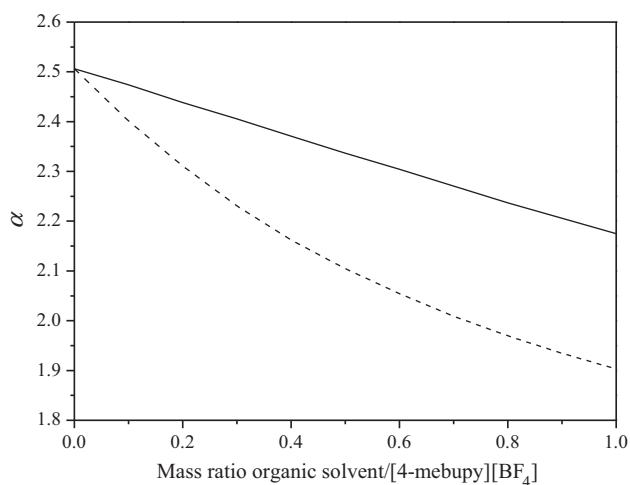


Fig. 8. Influence of the mass ratio organic solvent/IL on the relative volatility (α) of the ethylbenzene/styrene mixture at a pressure of 50 mbar and an ethylbenzene/styrene mass ratio of 4/6. (—) sulfolane; (---), NMP.

reboiler heat duty decreases with increasing NTS. The selected NTS for the blends sulfolane/IL and NMP/IL are 8 and 16, respectively. The reboiler heat duty decreases less than 1% if one extra stage is added, and this was used as the criterion to select the NTS. The total process was modelled with these parameters for the regeneration column. The required energy for the complete process with distillation as the regeneration technology with the blends sulfolane/IL and NMP/IL were 24 MW and 25 MW, respectively, which are in the same range as the other regeneration technologies.

4.8. ScCO₂ extraction

The proposed extractive distillation process with ScCO₂ extraction as the recovery technology is shown in Fig. 1f. In this recovery process, a large part (97%) of the styrene is recovered by the evaporator operating at mild conditions. The approach to calculate the energy requirements to compress the scCO₂ was followed as described in Section 3.3. First, the influence was determined of the organic concentration in the feed on the solvent capacity for the single stage extraction experiments using scCO₂ performed by Blanchard and co-workers [16]. In their manuscript no feed concentration is reported. However, this information is required to calculate the solvent capacity from their liquid–liquid equilibrium data. Therefore, the solvent capacity was calculated for several organic feed concentrations, which is shown in Fig. 10. This figure shows that the distribution increases with decreasing amount of organics in the feed. To calculate a best case scenario, the calculations were continued with a distribution coefficient of 0.765 that was calculated for low concentrations of the organics in the feed. It was calculated that a scCO₂ flow of 82 kg/s is required to recover the styrene from the IL [4-mebupy][BF₄] using the distribution coefficient and a mass balance over the scCO₂ extraction vessel. The energy requirements are 79 MW to compress the CO₂ to supercritical conditions [40]. This value is much larger compared to the other regeneration technologies, which have heating requirements in the range of 23–26 MW including the energy required for the extractive distillation column. Since the energy requirements for this process are much larger compared to the other regeneration processes, it was decided not to calculate the CAPEX for the scCO₂ process.

4.9. Comparison of different regeneration processes

The heat duty and refrigeration requirements for the processes using the different regeneration technologies are illustrated in

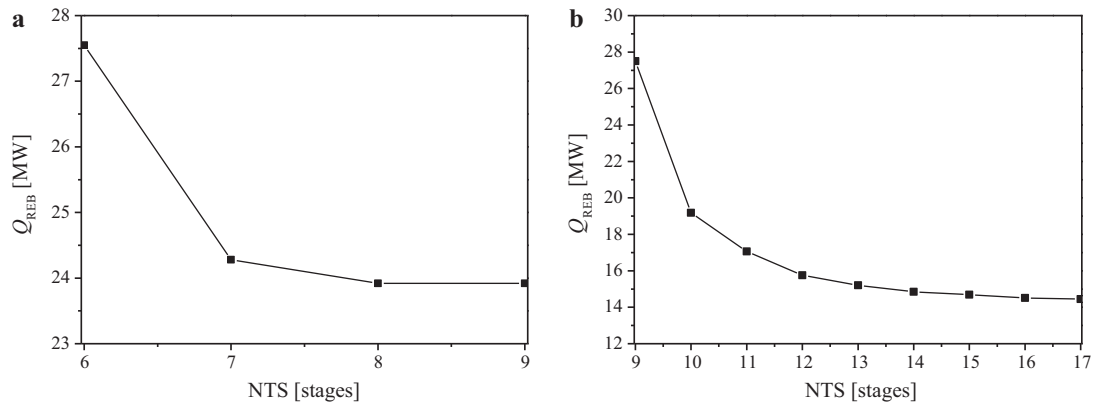


Fig. 9. Reboiler heat duty (Q_{REB}) as function of the number of theoretical stages (NTS) for the regeneration column using the solvent blends: (a) sulfolane/ionic liquid blend and (b) NMP/ionic liquid blend.

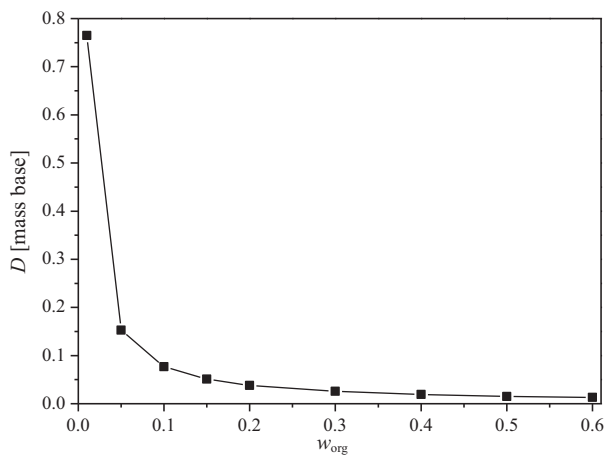


Fig. 10. The calculated solvent capacity (D) for different mass fractions of organics in the feed (w_{org}) from the liquid-liquid equilibrium data of the system benzene + [BMIM][PF₆] + ScCO₂ determined by Blanchard and co-workers [16].

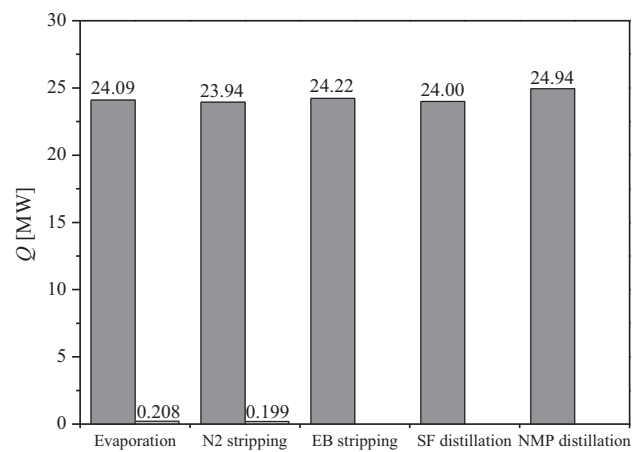


Fig. 11. Heat duty and refrigeration requirements for the regeneration processes. Grey bars, heat duty requirements; light grey bars, refrigeration requirements.

Fig. 11. The heat duties and refrigeration requirements were taken for the IL recycle purity of 99.9 wt% for the processes using the different regeneration technologies. This IL recycle purity gave the lowest energy requirements for all processes using the different regeneration technologies as described in Sections 4.4–4.6. From Fig. 11 it can be seen that there are no large differences

in energy requirements between the different regeneration processes. This can be explained by the low energy requirements for the regeneration technologies compared to the energy requirements for the total process, which is also explained in Sections 4.4–4.6. The OPEX and CAPEX were calculated for the extractive distillation column and the different regeneration processes, which are depicted in Fig. 12. From Fig. 12a it can be seen that there

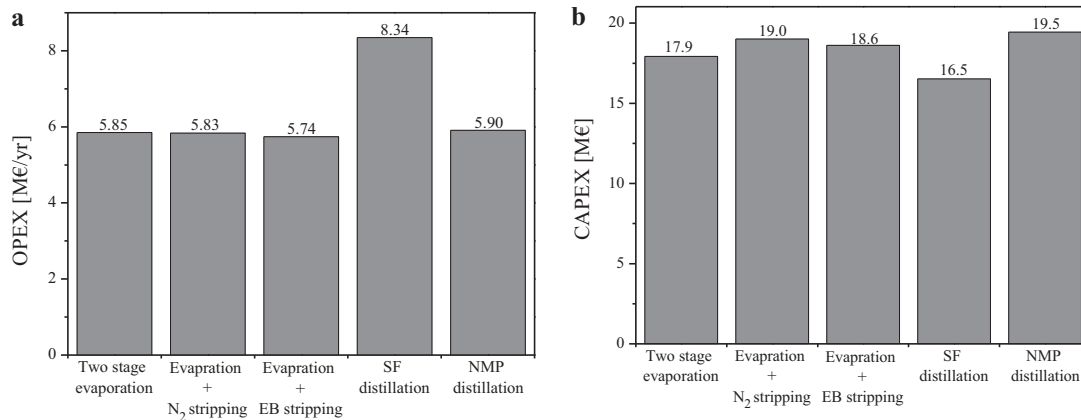


Fig. 12. (a) Operational expenditures (OPEX) regeneration processes. (b) Capital expenditures (CAPEX) regeneration processes. The first and second evaporator in the two stage evaporation recovery process operate at 11.1 and 2.6 mbar, respectively. The evaporator in the N₂ and EB stripping process operates also at 111 mbar.

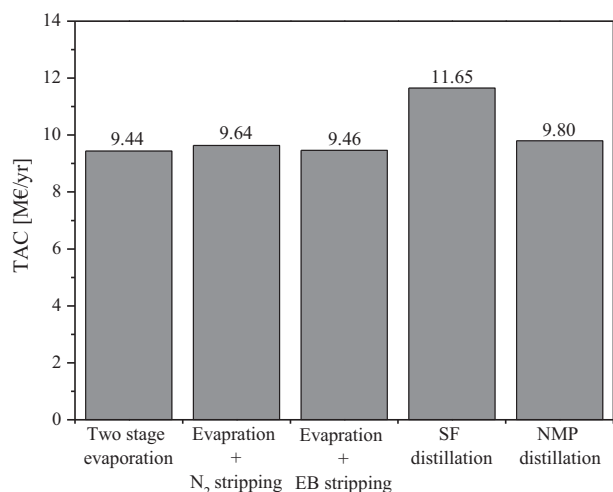


Fig. 13. Total annual costs (TAC) of the different regeneration processes.

are no large differences in OPEX between the different regeneration technologies, except for the distillation recovery technology using the sulfolane/IL blend, which has a significantly higher OPEX. This much larger OPEX for the sulfolane/IL blend compared to the NMP/IL blend for example can be explained by the higher required steam pressure, which needs to be used in the regeneration column using the sulfolane/IL blend. Medium pressure steam (10 bar) is required for this blend, whereas only low pressure steam (3.4 bar) is required for the NMP/IL blend. The differences in the required steam pressure can be explained by the higher reboiler temperature for the sulfolane/IL blend compared to the NMP/IL blend, which are 165.8 °C and 117 °C, respectively. These differences originate from the differences in boiling points of sulfolane (287.3 °C, [48]) and NMP (202 °C, [48]). Thereby, the regeneration using sulfolane as a co-solvent also exceeds the temperature limit of 130 °C. However, only the reboiler operates at this temperature, in which only very small amounts of styrene are present. The small differences in OPEX between the other processes can be explained by the low contribution of the OPEX of the regeneration technologies to the total OPEX of the process (1–3%). The differences are larger in the CAPEX, which is shown in Fig. 12b. The extractive distillation processes with the recovery technologies N₂ stripping and distillation with the blend MMP/IL give clearly the highest CAPEX. Distillation with the blend SF/IL would require the lowest CAPEX, but this regeneration technology has a much larger OPEX compared to the other options. The total annual costs (TAC = OPEX + 0.2CAPEX [19]) were calculated to evaluate the different recovery technologies. The calculation of the TAC is often used to finalize a conceptual design study. These results are depicted in Fig. 13, which shows the TAC for evaporation using very low pressures ($P < 10$ mbar) and stripping with ethylbenzene are slightly lower than the other recovery technologies. Therefore based on the TAC, the conclusion can be drawn that these two technologies are the most promising options to implement in the extractive distillation process for the separation of ethylbenzene from styrene. The chemical process industry is already familiar with both options. A more detailed technical feasibility study should elucidate whether these technologies indeed can be beneficial to implement in the current styrene production process. Both processes could also further be improved in terms of energy efficiency and capital investment by applying model based integrated optimization methods. This type of work was outside the scope of this study. A further optimization would also require a more extensive thermodynamic dataset.

5. Conclusions

Research was performed to evaluate several separation technologies to recover styrene monomer from the IL [4-mebupy][BF₄] to be implemented in the extractive distillation process for the separation of ethylbenzene from styrene. After a sensitivity analysis, an S/F ratio of 3.8 on mass base and 45 theoretical equilibrium stages were selected as the operational settings for the extractive distillation column. It was found that the IL recycle should be purified to at least 99.6 wt% to recycle this stream to the extractive distillation column. This purity could not be obtained using just an evaporator, which operates at mild conditions ($T = 130$ °C, $T_{\text{condenser}} = 20$ °C), and thus other regeneration technologies were required. The energy requirements for the other regeneration technologies were calculated after a sensitivity analysis of the regeneration processes including extractive distillation column. The OPEX, CAPEX, and TAC of the different processes show that evaporation using very low pressures ($P < 10$ mbar) and ethylbenzene stripping are the most promising technologies to recover the styrene monomer from the IL [4-mebupy][BF₄].

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