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Conceptual process design of extractive distillation processes for ethylbenzene/styrene separation

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ABSTRACT

In the current styrene production process the distillation of the close-boiling ethylbenzene/styrene mixture to obtain an ethylbenzene impurity level of 100 ppm in styrene accounts for 75–80% of the energy requirements. The future target is to reach a level of 1–10 ppm, which will increase the energy requirements for the distillation even further. Extractive distillation is a well-known technology to separate close-boiling mixtures up to high purities. The objective of this study was to investigate whether extractive distillation using ionic liquids (ILs) is a promising alternative to obtain high purity styrene. Three ILs were studied: [3-mebupy][B(CN)₄], [4-mebupy][BF₄], and [EMIM][SCN]. Extractive distillation with sulfolane and the current conventional distillation process were used as benchmark processes. The IL [4-mebupy][BF₄] is expected to outperform the other two ILs with up to 11.5% lower energy requirements. The operational expenditures of the [4-mebupy][BF₄] process are found to be 43.2% lower than the current distillation process and 5% lower than extractive distillation with sulfolane extractive distillations. However, the capital expenditures for the sulfolane process will be about 23% lower than those for the [4-mebupy][BF₄] process. Finally, the conclusion can be drawn from the total annual costs that all studied extractive distillation processes outperform the current distillation process to obtain high purity styrene, but that the ILs evaluated will not perform better than sulfolane.

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Keywords: Sulfolane; Ionic liquids; Extractive distillation; Ethylbenzene; Styrene; Conceptual design

1. Introduction

A typical 500,000 metric tonnes annually (mta) styrene production plant (Welch, 2001) contains an ethylbenzene/styrene distillation column with about 70 equilibrium stages, which operates at a reflux ratio of 7.1 to achieve an ethylbenzene impurity level in the final styrene product of 100 ppm (Chen, 2000). This column accounts for 75–80% of the total energy requirements in the current production process (Welch, 2001). The future target is to reach ethylbenzene impurity levels of 1–10 ppm. It is anticipated that the energy (and capital) requirements will increase even further if distillation is applied to obtain these higher purities. Obviously, an alternative technology is desired, which should replace the current distillation. A promising alternative is extractive distillation,

which is a well-known technology to decrease the operational and capital expenditures (OPEX and CAPEX) for the separation of close-boiling mixtures (Lee and Gentry, 1997; Gentry et al., 2004; Lei et al., 2005; Souders, 1964). Extractive distillation is already applied to produce high purity aromatics (Gentry et al., 2004). The commonly applied solvent sulfolane (Lei et al., 2005; Steltenpohl et al., 2005) is a promising organic solvent, which can increase the relative volatility of the ethylbenzene/styrene mixture up to 2.3 (Gentry et al., 2004; Jongmans et al., 2011a). Nevertheless, sulfolane has a significant vapor pressure and, therefore, can contaminate the final (high purity) styrene product. Ionic liquids (ILs) are often reported as promising alternatives for commonly applied organic solvents (Marsh et al., 2004; Meindersma et al., 2007; Giernoth, 2010; Beste et al., 2005), due to their negligible vapor pressure (Beste et al., 2005;

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Nomenclature

C_p	specific heat capacity, J/(g K)
D	solvent capacity
F	feed, kg
M_w	molecular weight, g/mole
P	pressure, Pa
Q	heat, MW
R	reflux ratio
S	solvent, kg
S_{ij}	selectivity
T	temperature, K
w	weight fraction
x	mole fraction

Greek symbols

α	relative volatility
η	viscosity, Pa s

Subscripts

REB	reboiler
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Abbreviations

CAPEX	capital expenditures
DIPPR	design institute for physical property data
EB	ethylbenzene
[EMIM][SCN]	1-ethyl-3-methylimidazolium thiocyanate
IL	ionic liquid
LLE	liquid–liquid equilibrium
[3-mebupy][B(CN) ₄]	3-methyl- <i>N</i> -butylpyridinium tetracyanoborate
[4-mebupy][BF ₄]	4-methyl- <i>N</i> -butylpyridinium tetrafluoroborate
mta	metric tonnes annually
MESH	material equilibrium summation heat
NRTL	non-random two liquid
NTS	number of theoretical stages
OPEX	operational expenditures
ppb	parts per billion
ppm	parts per million
SM	styrene monomer
VLE	vapor–liquid equilibrium

Jork et al., 2005; Lei et al., 2005). An IL combines the advantages of a solid salt (high separation ability) and liquid solvent (easy operation) (Lei et al., 2007). Moreover, ILs are also reported as designer solvents due to the many possible cation–anion combinations (Giernoth, 2010; Lei et al., 2007) by which high chemical and thermal stability (Marsh et al., 2004), and high capacity for aromatic components (Hansmeier et al., 2010) can be achieved.

We have demonstrated in the IL screening study that several ILs have a higher selectivity than sulfolane for the ethylbenzene/styrene mixture (Jongmans et al., 2011b). However, most (hydrophilic) ILs do not mix over the full composition range with aromatics, due to the low IL solubility in aromatics (Onink et al., submitted for publication). Therefore, the solvent capacity plays also an important role in extractive distillation processes. Liquid–liquid phase splitting should be avoided, because it decreases the process efficiency (Kyle and Leng, 1965; Kossack et al., 2008). The IL screening study showed a clear trade-off between the

solvent capacity and selectivity. The conceptual design study as presented in this study was carried out to elucidate whether the use of ILs in extractive distillation is beneficial compared to the traditional distillation and the extractive distillation using sulfolane. Moreover, the conceptual design study should determine which type of IL will be more efficient: an IL with high selectivity and low capacity, an IL with low selectivity and high capacity, or an IL with moderate selectivity and capacity. The ILs 3-methyl-*N*-butylpyridinium tetracyanoborate ([3-mebupy][B(CN)₄]), an IL with low selectivity and high capacity, 4-methyl-*N*-butylpyridinium tetrafluoroborate ([4-mebupy][BF₄]), an IL with moderate selectivity and capacity, and 1-ethyl-3-methylimidazolium thiocyanate ([EMIM][SCN]), an IL with high selectivity and low capacity, were selected to be studied in more detail. The molecular structures, molecular weights (M_w), solvent capacities on mass base (D), selectivities (S), specific heat capacity (C_p), and dynamic viscosity (η) of the ILs and the benchmark solvent sulfolane are listed in Table 1.

The conceptual process designs were made for three different ethylbenzene impurity levels: 100, 10, and 1 ppm. The separation of heavies from sulfolane/ILs that are also present in the feed to the separation section in the current production process (Ward and Robert, 2000), like cumene and styrene dimers/trimers for example, was not taken into account in this study. One or two stage evaporation was used, depending on the IL, as the IL recovery technology (Jongmans et al., submitted for publication). In the process design, first the extractive distillation column was optimized to find the optimal number of equilibrium stages (NTS), reflux ratio (R), and solvent-to-feed (S/F) ratio. This was followed by investigating the effect of different styrene concentrations in the IL recycle on the reboiler heat duty and to determine the minimum purity of the IL recycles to avoid the formation of two liquid phases in the extractive distillation column. Subsequently, the regeneration technologies were modeled followed by the implementation of a heat integration network to minimize heat losses. Finally, the OPEX, CAPEX, and total annual costs (TAC) were calculated for the different processes.

2. Process descriptions

In this section, the process flow diagrams of the distillation process, the extractive distillation process using sulfolane, and the extractive distillation processes using ILs are presented. The process diagrams are illustrated in Fig. 1.

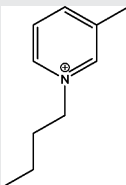
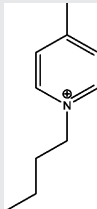
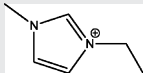
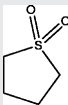
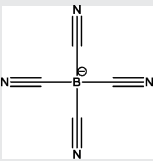


2.1. Current distillation process

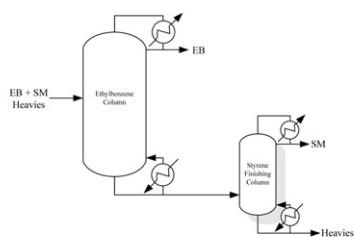
The process scheme of the current distillation process is shown in Fig. 1a. The ethylbenzene/styrene feed together with some heavies (Welch, 2001) is fed to the middle of the ethylbenzene distillation column. Ethylbenzene leaves the column via the top. The bottom stream, which contains styrene with some heavies, is fed to the styrene finishing column. In this column, the final styrene product is obtained at the top, and the heavies leave the column via the bottom. The styrene top product contains still some ethylbenzene impurities (currently ~ 100 ppm).

2.2. Extractive distillation process using sulfolane

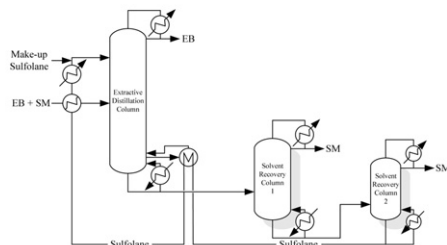
The process diagram of the extractive distillation process using sulfolane is illustrated in Fig. 1b. The

Table 1 – Properties of the selected ionic liquids.

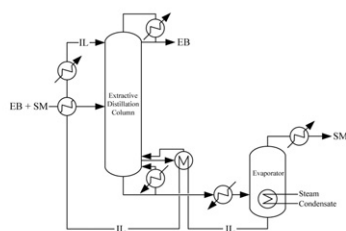
Ionic liquid	[3-Mebupy][B(CN) ₄]	[4-Mebupy][BF ₄]	[EMIM][SCN]	Sulfolane
Molecular structure				
				
M _w [g/mole]	265.12	237.05	169.25	120.17
D _{styrene} (Jongmans et al., 2011b)	0.592	0.414	0.229	^a
D _{ethylbenzene} (Jongmans et al., 2011b)	0.429	0.234	0.105	^a
S _{ij} (Jongmans et al., 2011b)	1.38	1.774	2.184	1.5–1.6 (Jongmans et al., 2011a)
C _p at 343.15 K [J/(gK)]	1.640 (Meindersma et al., 2011)	1.654 (Bandres et al., 2008)	1.773 (Ficke et al., 2010)	1.583 (Castagnolo et al., 1981)
η at 348.15 K [mPa s]	7.6 (Meindersma et al., 2011)	19.0 (Sanchez et al., 2009)	6.5 (Domanska et al., 2010)	3.86 (Al-Azzawi and Awwad, 1990)
^a Sulfolane is fully miscible with ethylbenzene and styrene.				



a. Process scheme current distillation process.



b. Process scheme extractive distillation process using sulfolane as a solvent. The first recovery column operates at 50 mbar, the second recovery column at 10 mbar.



c. Process scheme extractive distillation process with an evaporator.

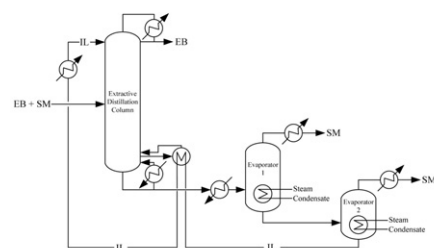
d. Process scheme extractive distillation process with two evaporators as regeneration technology. First evaporator is operating at mild conditions ($T = 130\text{ }^{\circ}\text{C}$, $T_{\text{condenser}} \geq 20\text{ }^{\circ}\text{C}$), the second evaporator at very low vacuum pressures ($P < 10\text{ mbar}$).

Fig. 1 – Process schemes of the different processes. EB: ethylbenzene; SM: styrene; IL: ionic liquid. (a) Process scheme current distillation process, (b) process scheme extractive distillation process using sulfolane as a solvent. The first recovery column operates at 50 mbar, the second recovery column at 10 mbar, (c) process scheme extractive distillation process with an evaporator and (d) Process scheme extractive distillation process with two evaporators as regeneration technology. 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 vacuum pressures ($P < 10\text{ mbar}$).

ethylbenzene/styrene feed and sulfolane are fed correspondingly to the middle and a few stages below the top of the extractive distillation column. Ethylbenzene leaves the extractive distillation column via the top, because sulfolane has less affinity for ethylbenzene (Jongmans et al., 2011a). Styrene and sulfolane leave the extractive distillation column via the bottom and are fed to the solvent recovery section. The solvent recovery section consists of two distillation columns. The second recovery column operates at lower pressures ($P < 50\text{ mbar}$) than the first recovery column ($P = 50\text{ mbar}$) to avoid temperatures higher than $130\text{ }^{\circ}\text{C}$ in the reboiler (Welch, 2001). Styrene is obtained at the top of both columns. The regenerated sulfolane

is cooled down and recycled to the top of the extractive distillation column. Heat integration was performed to minimize the heat losses by adding an extra reboiler at the bottom of the extractive distillation column and evaporating a fraction of the ethylbenzene/styrene feed. This type of heat integration is commonly applied in extractive distillation units (Gentry et al., 2004). One extra heat exchanger was required to cool down the sulfolane to the temperature of the top of the extractive distillation column. The sulfolane make-up stream accounts for the small solvent losses at the tops of the distillation columns.

2.3. Extractive distillation process using ionic liquids

The final process schemes for the extractive distillation processes using the three different ILs are illustrated in Fig. 1c and d. The feed and product streams to the extractive distillation column are similar to the process with sulfolane. However, the IL can be fed at the top stage due its negligible vapor pressure. Therefore, the IL can also be recovered by evaporation instead of distillation in the recovery section. The bottom stream from the extractive distillation column is warmed-up by a heat exchanger to reach the temperature of the first evaporator ($T \leq 130\text{ }^{\circ}\text{C}$; Welch, 2001, $P = 11.1\text{ mbar}$; Jongmans et al., submitted for publication), a second evaporator operating at even lower pressures ($P < 11.1\text{ mbar}$) might be necessary, which is illustrated in Fig. 1d. The condenser of the second evaporator uses refrigerant to condense the styrene. The recovered IL is recycled to the top of the extractive distillation column. Here, heat integration to minimize heat losses was performed as well.

3. Process modeling and operational and capital expenditures

This section provides the model choice, simulation package, modeling approach, model input, and the input for the calculation of the CAPEX and OPEX.

3.1. Equilibrium stage model

The various processes were modeled using an equilibrium stage model, which assumes physical equilibrium between the vapor and liquid phase (Poling et al., 2007). An equilibrium process model is sufficient for a first evaluation of the various processes. The equilibrium stage model is based on the MESH (Material, Equilibrium, Summation, and Heat balance) equations. The simulation package Aspen Plus[®] was used, which is often applied to model (extractive) distillation processes (Gomez and Gil, 2007; ASPEN Plus V7.2, 2011; Hömmerich and Rautenbach, 1998; Pinto et al., 2000). The RadFrac model was used to simulate the (extractive) distillation columns. The Boston and Britt algorithm was used to model the current distillation column, which is recommended for common two phase distillations (ASPEN Plus V7.2, 2011). The Newton algorithm, which is recommended for highly non ideal systems (ASPEN Plus V7.2, 2011; Baur et al., 2000), was used to model the extractive distillation columns and the solvent recovery column in the sulfolane extractive distillation process. The evaporators and the styrene finishing column in the current distillation process were modeled 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 (Poling et al., 2007). The vapor phase was modeled as an ideal gas, because the processes were all modeled at deep vacuum and consisted mainly of ethylbenzene and styrene, which are similar components. The pure component vapor pressures of ethylbenzene (Jongmans et al., 2011a), styrene (Jongmans et al., 2011a), and sulfolane (Gmehling and Onken, 1977) were calculated by the Antoine equation. A vapor pressure of zero was attributed to the three ILs, because they have a negligible vapor pressure. The non-ideal behavior in the liquid phase was calculated by the NRTL model (Poling et al., 2007; Renon and Prausnitz, 1968). The binary NRTL parameters were taken from previous work (Jongmans et al., 2011a, 2012a,b,c). The liquid heat capacity is another important physical property in the design of an extractive distillation process, because it determines the energy requirements for solvent heating/cooling (Souders, 1964). The specific heat capacity for the components was calculated by the DIPPR (Design Institute for Physical Properties) equation. The parameters for ethylbenzene, styrene, and sulfolane were taken from the Aspen Plus databank. The DIPPR parameters for the ILs [3-mebupy][B(CN)₄] (Meindersma et al., 2011), [4-mebupy][BF₄] (Bandres et al., 2008), and [EMIM][SCN] (Ficke et al., 2010) were taken from the open literature.

3.3. Model input

3.3.1. Feed conditions, purity requirements, and process conditions

The data provided in the patent of Welch (2001) were used as input for the model of the current distillation process. The ethylbenzene/styrene feed to the distillation and extractive distillation processes was 100 metric tonnes/h, with a styrene concentration of 60 mole% (Welch, 2001). The ethylbenzene/styrene feed entered the columns in all processes as a saturated liquid. The ethylbenzene product obtained at the top of the distillation/extractive distillation columns was set to 98.3 mole% (Welch, 2001). The final styrene product was modeled for several ethylbenzene impurity levels: 100, 10, and 1 ppm. A mass balance was applied to calculate the top and bottom flows of the columns. The temperature at which sulfolane and the three ILs enter the extractive distillation column were set to the temperature of the tray at which they are fed. The condenser pressures in the distillation/extractive distillation columns were set to 50 mbar to keep the temperature in the column low, thereby minimizing styrene polymerization. The first recovery column in the sulfolane process was modeled at 50 mbar. A pressure of 10 mbar was used in the second recovery column to keep the reboiler temperature below 130 °C. The Sulzer structured packing Mellapak 250X was selected as internal, because of its low pressure drop. This packing type is often applied in ethylbenzene/styrene splitters (Welch, 2001; Ward and Robert, 2000). A thermosyphon reboiler was used in the model, which is often applied to distill thermally sensitive components (Welch, 2001; Perry and Green, 1997).

3.3.2. Current distillation process

The reflux ratio and number of theoretical stages (NTS) both have a strong effect on the performance of a distillation column (Perry and Green, 1997; Doherty and Knapp, 2000). Both were varied to obtain the desired ethylbenzene impurity

levels of 100, 10, and 1 ppm in the final styrene product. First, the reflux ratio was kept constant and the NTS were varied by a design spec in Aspen Plus. This was followed by keeping the NTS constant and varying the reflux ratio. The ethylbenzene impurity levels in the bottom were set as the target. Finally, the energy requirements were calculated for the different scenarios. The energy requirements for the styrene finishing column were determined by calculating the heat duty required for evaporating the styrene present in the bottom stream from the ethylbenzene/styrene distillation column.

3.3.3. Extractive distillation using sulfolane

First, the sulfolane feed stage was set to keep the sulfolane concentration in the ethylbenzene top stream below 1 ppm. The organic feed was set manually at the stage where the ethylbenzene/styrene ratio was similar to the ethylbenzene/styrene feed ratio (40/60). The extractive distillation column was optimized by varying the S/F ratio, NTS, and reflux ratio (Lei et al., 2005; Sucksmith, 1982). For each S/F ratio (range 1–5), the NTS was varied from 50 to 85 with a step change of 5, and the minimum required reflux ratio to obtain the desired purity of styrene in the bottom stream was calculated by a design spec.

Subsequently, the bottom stream from the extractive distillation was used as feed stream in the optimization of the solvent recovery columns. This was done by varying the NTS in the range 8–18 with a step change of 1 and by calculating the required reflux ratio via a design spec for both recovery columns. Here, the impurity levels of ethylbenzene and sulfolane in the styrene exit stream were set as the target. The sum of these ethylbenzene and sulfolane concentrations was set at either 100, 10, or 1 ppm, according to the desired purity. This implies that the sulfolane concentration in the final styrene product was almost negligible (<10 ppb) in all cases. The styrene mass fraction in the bottom stream of the first recovery column was set at 0.0175 to keep the reboiler temperature below 130 °C. The styrene mass fraction in the bottom stream of the second solvent recovery column was set at 0.001, because low styrene concentrations in the recycle to the extractive distillation column are preferred (Jongmans et al., submitted for publication). Finally, the total model was simulated by closing the sulfolane recycle and applying heat integration. For the heat integration, a logarithmic temperature difference of 10 K was assumed between the hot and cold stream (Seider et al., 2004).

3.3.4. Extractive distillation using ionic liquids

The same parameters were varied as for the extractive distillation process with sulfolane to find the optimized settings. However, due to the miscibility gap between the ILs and the ethylbenzene/styrene (Jongmans et al., 2011b), first the minimum required S/F ratio was determined for the three different ILs to avoid multiple liquid phases at any stage in the extractive distillation column. Subsequently, the S/F ratio was varied from the determined minimum required S/F ratio up to 1.5–2.5 times the minimum required S/F ratio, depending on the IL. The NTS were varied in the range 35–70 with a step change of 5. The reflux ratio was calculated by a design spec as well to obtain the desired purity of styrene in the bottom stream.

After finding the optimal settings for the extractive distillation columns for the three ILs, the effect of the styrene concentration in the IL recycle on the extractive distillation was examined. This sensitivity analysis was required to find the minimum IL purity, which needs to be obtained in the

Table 2 – Cost factors for the operational expenditures.

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
Dutch Association of Cost Engineers (2011) and Seider et al. (2004).	

IL regeneration section. The styrene concentration in the IL recycle was varied from 0 to 1.5 wt%, depending on the IL. The reflux ratio was varied in order to minimize the energy consumption of the process, while still fulfilling the purity requirements with respect to the top and bottom products using a design spec.

Next, the maximum purity that can be obtained with an evaporator using mild conditions ($P = 11.1$ mbar, $T = 130$ °C, Jongmans et al., submitted for publication) was determined. An extra evaporator using very low vacuum pressures ($P < 10$ mbar) was modeled, when the IL purity specification could not be reached by the evaporator using mild conditions. Finally, the whole process was modeled by closing the IL recycle and applying a heat integration.

3.4. OPEX, CAPEX, and TAC

The OPEX, CAPEX, and TAC were determined to compare the different processes. The OPEX were calculated from the energy requirements provided by the Aspen Plus simulations using a running time of 8400 h per year (Dutch Association of Cost Engineers, 2011). The applied cost factors to estimate the OPEX are shown in Table 2. The plant location and (possible) solvent purge costs were not taken into account. The Aspen Plus Economic Analyzer was applied to calculate the CAPEX. The diameter and column heights of the (extractive) distillation columns were calculated in Aspen Plus using the Packing Sizing tool (ASPEN Plus V7.2, 2011). Standard overall heat transfer coefficients (Richardson et al., 2002) were used to calculate the areas of the shell-and-tube heat exchangers. A forced circulation and falling film evaporator were selected correspondingly for the first and second evaporator in the IL recovery process, which are both often applied for thermally sensitive components (Perry and Green, 1997). The purchase costs of pumps were not taken into account. It was assumed that refrigerant, steam, etc. are already available at the plant location. Stainless Steel 316 was selected as the material, because ILs are known to be slightly corrosive fluids (Arenas and Reddy, 2003; Uerdingen et al., 2005). Aromatics and sulfolane were both considered as non-corrosive fluids (Stewart and Minnear, 2011). Therefore, ordinary carbon steel was selected as the material to evaluate the current distillation process and the process using sulfolane. The total solvent investment was calculated from the total solvent hold-up and the price per kg. The assumption was made that the ILs cost 25 €/kg (Wasserscheid, 2008; Meindersma and de Haan, 2008), but the price was also varied up to 200 €/kg to investigate the contribution of the IL price to the total CAPEX. A price of 2.78 €/kg was taken for sulfolane (DIY Trade, 2011). The TAC were

calculated by summing up the OPEX and 20% of the CAPEX (Seider et al., 2004).

4. Results

The results from the process models of the different processes are presented in this section. First the results for the current distillation process are discussed, followed by the extractive distillation process using sulfolane. Next, the results are discussed for the extractive distillation processes using the different ILs. Finally, an overview is provided of the different technologies, which is based on the energy requirements, OPEX, CAPEX, and TAC.

4.1. Distillation

The process scheme of the current distillation process is shown in Fig. 1a. In order to check the reliability of the simulated process, a base case scenario based on the patent by Welch (2001) was simulated for an ethylbenzene impurity level of 100 ppm. The required reflux ratio and NTS were 7.1 and 70, respectively. This corresponds to the data provided in the patent by Welch (2001). In Fig. 2a, the required NTS and reboiler heat duty are illustrated as function of the ethylbenzene impurity level at a constant reflux ratio of 7.1. At higher purity constraints (10 ppm and 1 ppm, respectively), the required NTS were 81 and 93, meaning that the NTS increases with decreasing impurity level. This relationship can be derived from the Fenske equation (Fenske, 1932). Moreover, Fig. 2a shows that the reboiler heat duty slightly increases with decreasing impurity level. This trend can be explained by the higher temperatures in the bottom/reboiler of the distillation column at lower ethylbenzene impurity level, because more stages were required and thereby the pressure drop increases across the column. Moreover, the distillate rate slightly increases, and thereby the amount to evaporate, with decreasing ethylbenzene impurity level, which follows from the mass balance.

Fig. 2b shows the required reflux ratio and reboiler heat duty as function of the ethylbenzene impurity level at a constant NTS of 70. The reflux ratio and reboiler heat duty both strongly increase with decreasing ethylbenzene impurity level, which is common for distillation units (Doherty and Knapp, 2000). For an ethylbenzene impurity level of 10 and 1, reflux ratios are required of 8.7 and 12, respectively.

A reboiler heat duty of 6.6 MW was required for the styrene finishing column. The sum of the energy requirements presented in Fig. 2a and the reboiler heat duty of the styrene finishing column was used to compare the extractive distillation processes to the current distillation process, because varying the NTS to obtain higher styrene purities requires lower heat duties than varying the reflux ratio. More stages will require a larger CAPEX. However, a higher reflux ratio, and thus keeping NTS constant (see Fig. 2b), results in much higher internal liquid and vapor flows. Thereby, a much larger column diameter is required, which also increases the CAPEX.

4.2. Extractive distillation process using sulfolane

4.2.1. Extractive distillation column

The results from the optimization of the extractive distillation process for an ethylbenzene impurity level of 100 ppm are depicted in Fig. 3. The trends were similar for impurity levels of 10 and 1 ppm, but these were not depicted to keep the figure comprehensive. It was required to feed the

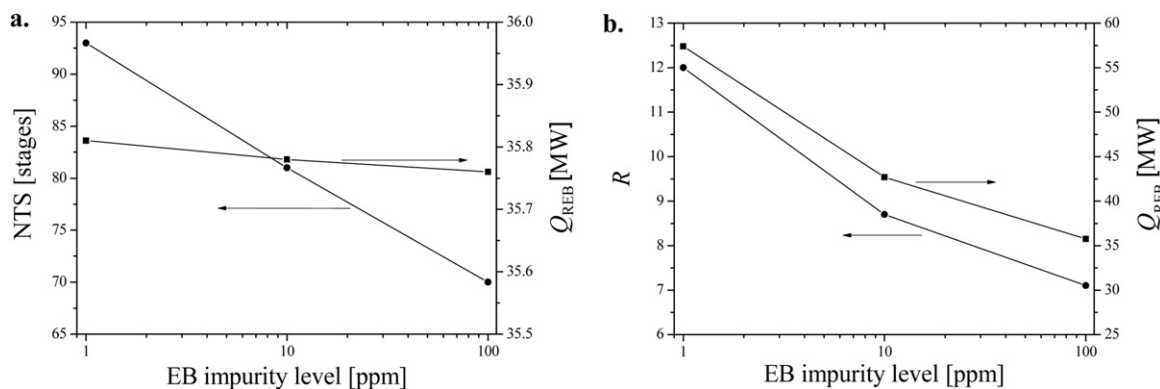


Fig. 2 – (a) Required number of equilibrium stages (NTS) and reboiler heat duty (Q_{REB}) as function of the ethylbenzene impurity level using a constant reflux ratio of 7.1. (b) Required reflux ratio (R) and reboiler heat duty (Q_{REB}) as function of the ethylbenzene impurity level using a constant number of stages of 70.

sulfolane at stage number 8 to keep the sulfolane concentration in the ethylbenzene top product below 1 ppm. Fig. 3a shows that the reflux ratio of the extractive distillation column decreases with increasing S/F ratio, which is a common trend for extractive distillation columns (Sucksmith, 1982). The relative volatility increases with increasing S/F ratio (Jongmans et al., 2011a), and thereby the reflux ratio can be decreased to obtain the same bottom and top purity. However, the reflux ratio decreases stronger at lower S/F ratios with increasing S/F ratio compared to higher S/F ratios, which originates from the dependency of the relative volatility on the S/F ratio (Jongmans et al., 2011a). Fig. 3b displays the reboiler heat duty of the extractive distillation column, which decreases with increasing S/F in the low S/F range. The reboiler heat duty approaches a minimum around a S/F of 2.5–3, depending on the NTS. The energy requirements in the reboiler are mainly used for evaporation (to obtain a certain boil up rate) and for solvent heating (Sucksmith, 1982). The energy required for evaporation decreases with increasing S/F ratio, which is a result from the decrease of the reflux ratio. However, the amount required for solvent heating increases linearly with increasing S/F ratio. So, the energy requirements for evaporation are dominant at low S/F ratios, but the amount required for solvent heating becomes more and more dominant at higher S/F ratios. For example at the S/F ratios of 1 and 5, the corresponding solvent heating energy requirements are about 3 and 32% of the total

energy requirements, respectively. Fig. 3 also illustrates that the reflux ratio and the reboiler heat duty both decrease with increasing NTS. However, from Fig. 3b can be seen that the reboiler heat duty does not decrease notably at a certain NTS, because the minimum reflux ratio is approached to obtain a certain top and bottom purity. An optimal NTS of 65, 70, and 75 were found for the ethylbenzene impurity levels of 100, 10, and 1 ppm, respectively. At these NTS, the reboiler heat duty decreases less than 1% compared to 5 stages less, which was used as the criterion to select the optimal NTS. The next step was to model the regeneration column, which is explained in the next section.

4.2.2. Regeneration column

Varying the S/F ratio in the extractive distillation column affects the requirements for the recovery columns as well. Therefore, the regeneration columns were modeled for several sulfolane/styrene ratios to investigate whether this ratio has a large effect on the reflux ratio and the reboiler heat duty of the solvent recovery columns. The results for these two parameters for the first recovery column as function of the S/F ratio of the extractive distillation column (i.e. sulfolane/styrene ratio) and NTS of the recovery column are displayed in Fig. 4 for an ethylbenzene impurity level of 100 ppm. The trends for 10 and 1 ppm and the second recovery column were similar to those for 100 ppm and the first recovery column, but are not plotted

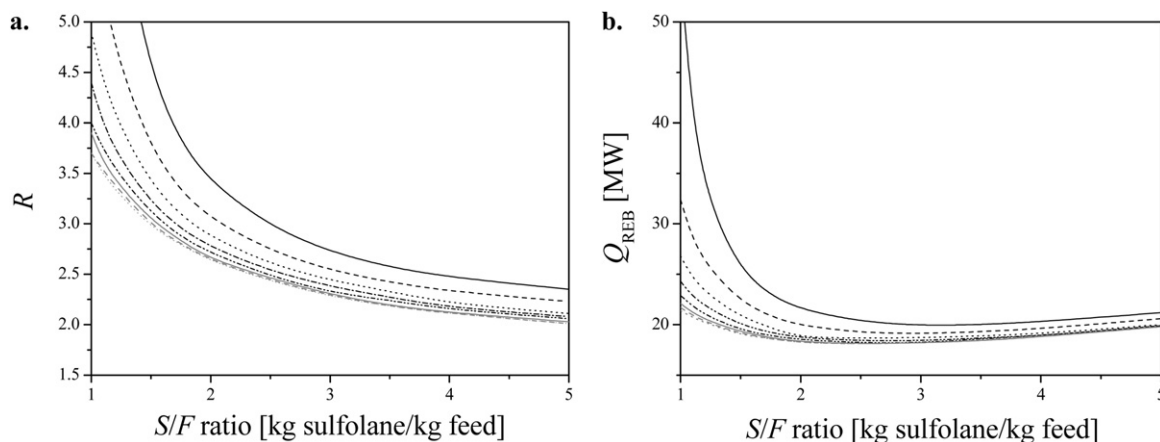


Fig. 3 – (a) Reflux ratio (R) of the extractive distillation column using sulfolane as function of S/F ratio and number of equilibrium stages (NTS) for an ethylbenzene impurity level of 100 ppm. (b) Reboiler heat duty Q_{REB} of the extractive distillation column as function of S/F ratio and NTS for an ethylbenzene impurity level of 100 ppm. (—) NTS = 50; (– –) NTS = 55; (· · ·) NTS = 60; (– · –) NTS = 65; (– · – ·) NTS = 70; (— · —) NTS = 75; (— · — ·) NTS = 80; (· · ·) NTS = 85.

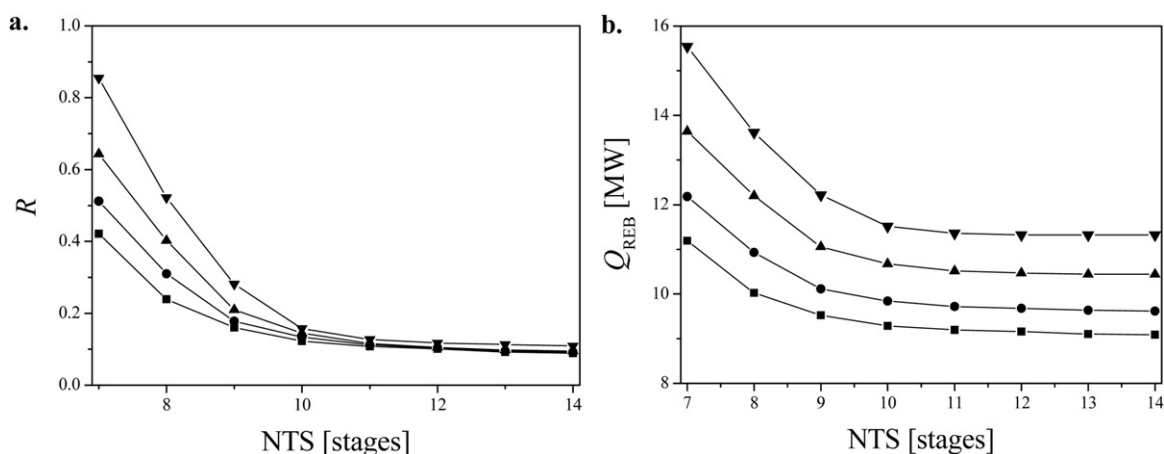


Fig. 4 – (a) Reflux ratio (R) of the first sulfolane regeneration column as function of S/F ratio of the extractive distillation column and number of equilibrium stages (NTS). (b) Reboiler heat duty Q_{REB} of the regeneration column of the extractive distillation column as function of S/F ratio of the extractive distillation column and NTS. (■) $S/F = 1$; (●) $S/F = 2$; (▲) $S/F = 3$; (▼) $S/F = 4$.

to keep the figure comprehensive. The reflux ratio, and consequently the reboiler heat duty both decrease with increasing NTS, which is typical behavior for distillation columns (Doherty and Knapp, 2000; Perry and Green, 1997; Seider et al., 2004). Fig. 4 also displays that the reflux ratio increases with increasing sulfolane/styrene ratio (i.e. increasing S/F ratio). The higher reflux ratio is required to maintain the amount of sulfolane in the final styrene product below 10 ppb. The reflux ratio is hardly dependent on the styrene/sulfolane ratio at high NTS (>11–12) and approaches the minimum reflux ratio. The low reflux ratios ($R < 0.2$) are a result from the large boiling point difference between styrene ($T_b = 145^\circ\text{C}$, Lide and Haynes, 2009) and sulfolane ($T_b = 287.3^\circ\text{C}$, Lide and Haynes, 2009). The reboiler heat duty, however, is strongly dependent on the sulfolane/styrene ratio, which is illustrated in Fig. 4b. The reboiler heat duty increases with increasing sulfolane/styrene ratio, because the amount required for solvent heating increases linearly with increasing sulfolane/styrene ratio. An optimum NTS of 12, 13, and 14 were selected for the first sulfolane regeneration column for the ethylbenzene impurity levels of 100, 10 and 1 ppm, respectively. An optimum NTS of 8 was selected for the second recovery column, independent of the ethylbenzene impurity level. At these NTS, the reboiler heat duty decreases less than 1% compared to 1 stage less, which was used as the criterion to select the optimal NTS.

4.2.3. Heat integration

The results of the total process model with the different heat integration steps are illustrated in Fig. 5a. The solid lines in Fig. 5a clearly demonstrate that the S/F ratio has a strong effect on the total required reboiler heat duty. The minimum in reboiler heat duty is around a S/F ratio of 1.75 for the different impurity levels if no heat integration would be performed. Fig. 5a also shows that the reboiler heat duty increases with decreasing ethylbenzene impurity levels, which was also the case for the current distillation process (see Section 4.1). However, the differences between the three impurity levels are not very large, which originates from the larger amount of stages selected for the lower ethylbenzene impurity levels. The final conclusion, which can be drawn from Fig. 5a is that the heat integration has a tremendous effect on the total required reboiler heat duty (Gentry et al., 2004), which is indicated with the dashed and dotted lines in Fig. 5a. For example, 95% of the

heat required for solvent heating can be recovered by applying heat integration on the reboiler of the extractive distillation column and evaporating a part of the organic feed stream at an S/F ratio of 3 and an ethylbenzene impurity level of 100 ppm. The OPEX were calculated for the total extractive distillation process including the heat integrations for different S/F ratios to determine the optimal S/F ratio. These results are displayed in Fig. 5b for the three different impurity levels. There is a clear minimum in OPEX at a S/F ratio of 2.5–3, depending on the required impurity level. Normally, the OPEX are linearly dependent on the required heating and cooling duties. However, chilled cooling water is required in the condenser of the second recovery column to condense the styrene, which requires more OPEX compared to normal cooling water (see Table 2). The cooling requirements in this condenser increase with increasing S/F ratio, because more styrene needs to be recovered in the second recovery column at higher S/F ratios. Hence, a minimum exists in OPEX at a S/F ratio of 2.5–3.

4.3. Extractive distillation processes using ionic liquids

4.3.1. Extractive distillation columns

The results for the optimization of the extractive distillation column for the ILs [3-mebupy][B(CN)₄], [4-mebupy][BF₄], and [EMIM][SCN] are illustrated respectively in Figs. 6–8 for an ethylbenzene impurity level of 100 ppm. The trends for 10 and 1 ppm were similar, but not included for readability reasons. Where the S/F ratio was not constrained by any liquid–liquid miscibility gap in the case of sulfolane, a liquid–liquid miscibility gap does exist in all processes using ILs resulting in a certain minimum S/F ratio required to maintain a homogeneous liquid phase. The minimum S/F ratios are 1.5, 3.8, and 8.4 for the ILs [3-mebupy][B(CN)₄], [4-mebupy][BF₄], and [EMIM][SCN], respectively. It can be seen in Fig. 6a (results for [3-mebupy][B(CN)₄]), that for an increasing S/F ratio, starting from the minimum S/F ratio of 1.5, the required reflux ratio to satisfy the purity constraints reduces. This trend is common, since the relative volatility increases with increasing S/F ratio, which was also observed for the sulfolane process. However, because a rather large minimum S/F ratio is required to obtain a homogeneous liquid phase, the addition of extra IL does not result in a very strong decrease of the reflux ratio, because adding extra IL above the minimum required S/F ratio

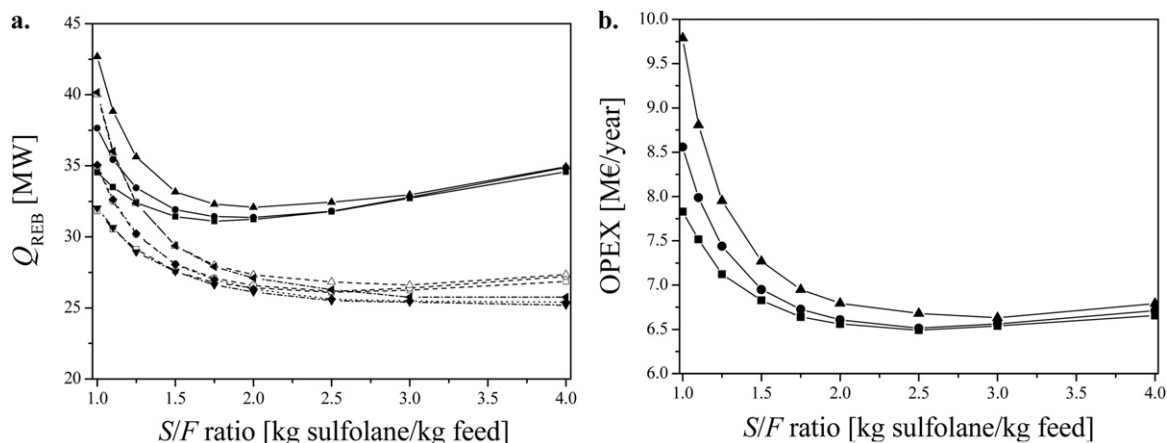


Fig. 5 – (a) Total reboiler heat duty (Q_{REB}) as function of S/F ratio and ethylbenzene impurity levels. No heat integration: (■) 100 ppm; (●) 10 ppm; (▲) 1 ppm, heat integration on reboiler: (□) 100 ppm; (○) 10 ppm; (△) 1 ppm. Heat integration on reboiler + feed [(▼) 100 ppm; (◆) 10 ppm; (◄) 1 ppm]. (b) Operational expenditures (OPEX) of the total extractive distillation process as function of S/F ratio and ethylbenzene impurity level. (■) 100 ppm; (●) 10 ppm; (▲) 1 ppm.

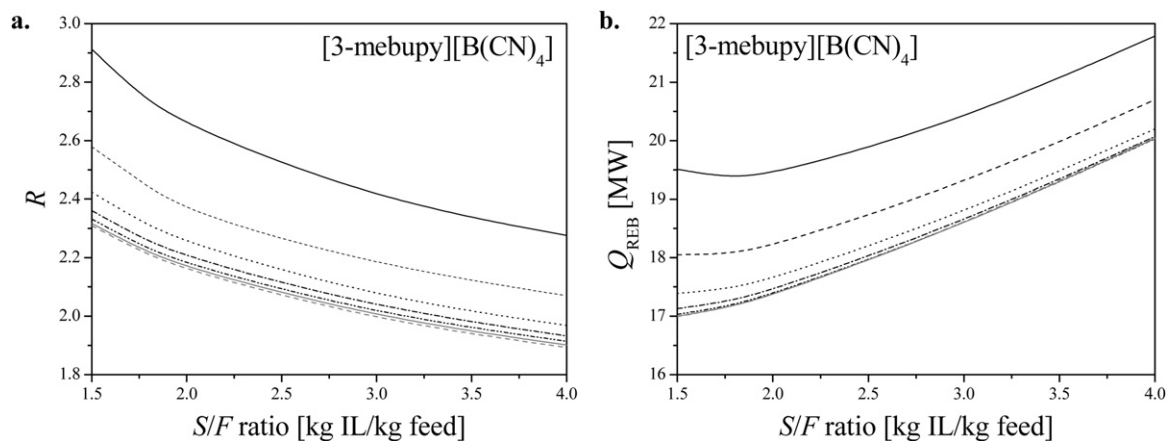


Fig. 6 – (a) Reflux ratio (R) of the extractive distillation column as function of S/F ratio and number of equilibrium stages (NTS) for the IL [3-mebupy][B(CN)₄]. (b) Reboiler heat duty Q_{REB} of the extractive distillation column as function of S/F ratio and NTS for the IL [3-mebupy][B(CN)₄]. (—) NTS = 40; (—) NTS = 45; (···) NTS = 50; (---) NTS = 55; (---) NTS = 60; (---) NTS = 65; (---) NTS = 70.

does not result in a significant increase of the relative volatility. From Fig. 6a and b, it follows that although the reflux ratio decreases with increasing S/F ratio, the required energy in the reboiler increases. The increased heat duty with increasing S/F ratio originates from the larger amount of energy required for solvent heating with increasing S/F ratio. The optimum

S/F ratio is thus the minimum ratio to maintain a single homogeneous liquid phase in the column. The results for [4-mebupy][BF₄] showed comparable trends, and also the absolute amounts of energy required in the reboiler are very comparable (see Fig. 7). However, due to the homogeneous liquid phase constraint, more solvent is needed. Even more

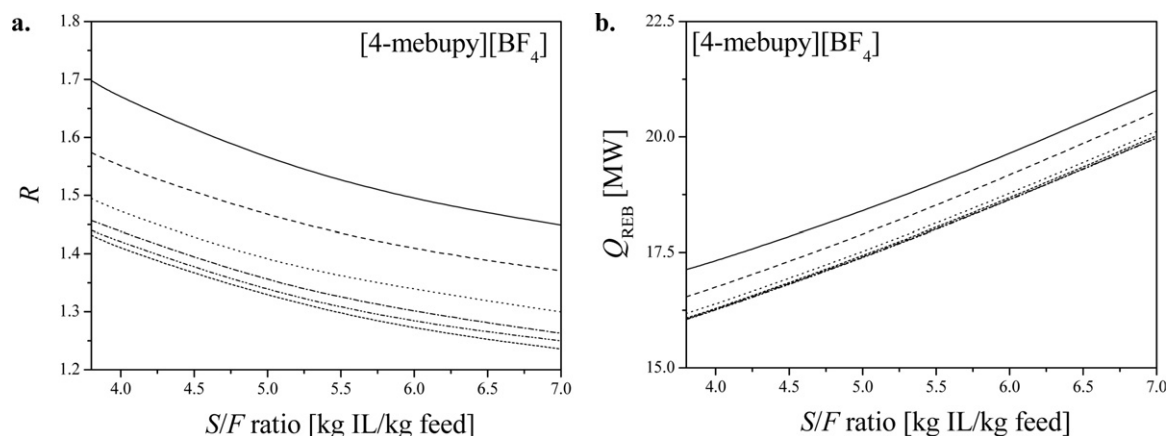


Fig. 7 – (a) Reflux ratio (R) of the extractive distillation column as function of S/F ratio and number of equilibrium stages (NTS) for the IL [4-mebupy][BF₄]. (b) Reboiler heat duty Q_{REB} of the extractive distillation column as function of S/F ratio and NTS for the IL [4-mebupy][BF₄]. (—) NTS = 35; (—) NTS = 40; (···) NTS = 45; (---) NTS = 50; (---) NTS = 55; (···) NTS = 60.

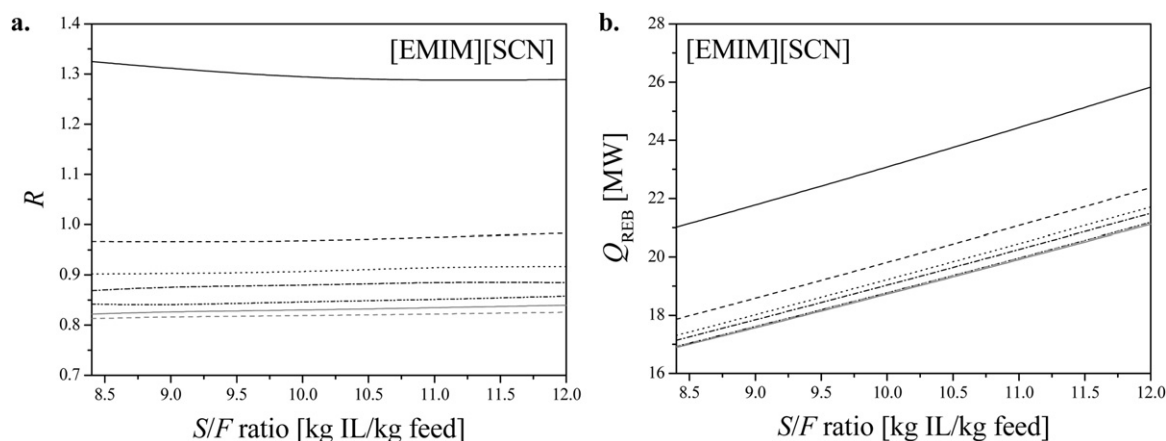


Fig. 8 – (a) Reflux ratio (R) of the extractive distillation column as function of S/F ratio and number of equilibrium stages (NTS) for the IL [EMIM][SCN]. (b) Reboiler heat duty Q_{REB} of the extractive distillation column as function of S/F ratio and NTS for the IL [EMIM][SCN]. (—) NTS = 20; (—) NTS = 25; (···) NTS = 30; (—) NTS = 35; (—) NTS = 40; (—) NTS = 45; (—) NTS = 50.

solvent is required in the case of [EMIM][SCN], as displayed in Fig. 8. Here, the minimum S/F ratio is already so high, that there is hardly any effect of the S/F ratio on the required reflux ratio visible. Here again, the absolute amount of energy required in the reboiler is comparable with the other ILs.

When comparing the reflux ratios in the IL based processes with each other, it follows that the lowest reflux ratios were required for the IL [EMIM][SCN] and the largest reflux ratios for the IL [3-mebupy][B(CN)₄]. This result was expected, based on the selectivities of the three ILs for the ethylbenzene/styrene mixture (see Table 1), which decrease in the order of [EMIM][SCN] > [4-mebupy][BF₄] > [3-mebupy][B(CN)₄]. The reflux ratio is dependent on the relative volatility (Underwood, 1932), which is subsequently dependent on the solvent selectivity (Kyle and Leng, 1965; Yin et al., 2010). The differences in selectivity apparently do not yield large differences in energy requirements of the reboiler at the optimized S/F conditions, but do have a significant effect on the NTS that is required.

With respect to variation of the NTS, Figs. 6–8 also display that the reflux ratio and thereby the reboiler heat duty decrease with increasing NTS. The same trend was observed for sulfolane. The optimal selected NTS for the three different ILs and the different ethylbenzene impurity levels are illustrated in Fig. 9a. A lower amount of NTS are required for the ILs compared to the current distillation and the sulfolane extractive distillation process. Even for the IL [3-mebupy][B(CN)₄], which has a lower selectivity than sulfolane, less NTS are required compared to sulfolane, because the IL can be fed at the top stage of the extractive distillation column. The required NTS for the different ILs decrease in the order of: [3-mebupy][B(CN)₄] > [4-mebupy][BF₄] > [EMIM][SCN]. This trend was also expected based on the selectivities of the three ILs (see Table 1). Moreover, Fig. 9a shows that more stages are required for lower ethylbenzene impurity levels, which was also observed for the distillation and sulfolane extractive distillation process.

The required reboiler heat duties of the extractive distillation column for the three ILs with the optimal selected NTS are displayed in Fig. 9b. Fig. 9b shows that the lowest amount of energy is required for the IL [4-mebupy][BF₄]. However, there is not a large difference in required reboiler heat duty between the three ILs. As explained above, the reboiler heat duty is dependent on the energy required for evaporation and solvent heating, which are related to the required reflux ratios

and S/F ratios. These energy requirements for solvent heating and evaporation are also displayed in Fig. 9b. The largest heat duties for solvent heating are required for the IL [EMIM][SCN], which can be explained by the larger required S/F ratio and its slightly higher specific heat capacity (see Table 1) compared to the other two ILs. However, [EMIM][SCN] requires the lowest heat duty for evaporation, which corresponds to the results for the required reflux ratios for the three ILs. [3-Mebupy][B(CN)₄] requires low amounts of energy for solvent heating, but high amounts for evaporation. [4-Mebupy][BF₄] requires average heat duties for solvent heating and evaporation. These results originate directly from the differences in solvent capacity and selectivity of the three ILs (see Table 1). Finally, the conclusion can be drawn that none of the ILs clearly outperforms the other ILs based on the energy requirements of the extractive distillation column. However, there is a difference in required NTS, which will have an effect on the required CAPEX, which is discussed later on in this manuscript. Therefore, it is not possible to already conclude if an IL with a high solvent capacity and low selectivity is for example better than an IL with a low solvent capacity and high selectivity. Therefore, the regeneration section was also modeled for the three ILs and the three different ethylbenzene impurity levels, which is explained in the next section.

4.3.2. Regeneration column

First, the influence of different styrene concentrations in the IL recycle on the reflux ratios and reboiler heat duties were investigated for the three ILs. The results from this sensitivity analysis are illustrated in Fig. 10. Fig. 10 shows that the reflux ratios (left y-axis) and thereby also reboiler heat duties (right y-axis) both increase with increasing styrene concentration in the IL recycle for all three ILs. A fraction of the added styrene in the IL recycle evaporates at the top stage, where the IL recycle is fed to the extractive distillation column. Therefore, the reflux ratio must increase to maintain the same ethylbenzene purity ($x_{EB} = 98.3$ mole%) at the top of the extractive distillation column. From the sensitivity analysis, the conclusion can be drawn that a styrene concentration in the IL recycle higher than 1.4, 0.4, and 0.24 wt% should be avoided for the ILs [3-mebupy][B(CN)₄], [4-mebupy][BF₄], and [EMIM][SCN], respectively. When styrene is added via the recycle, a higher reflux ratio is required to maintain the top purity of the extractive distillation column. This will decrease the IL/organic ratio in the column, and will

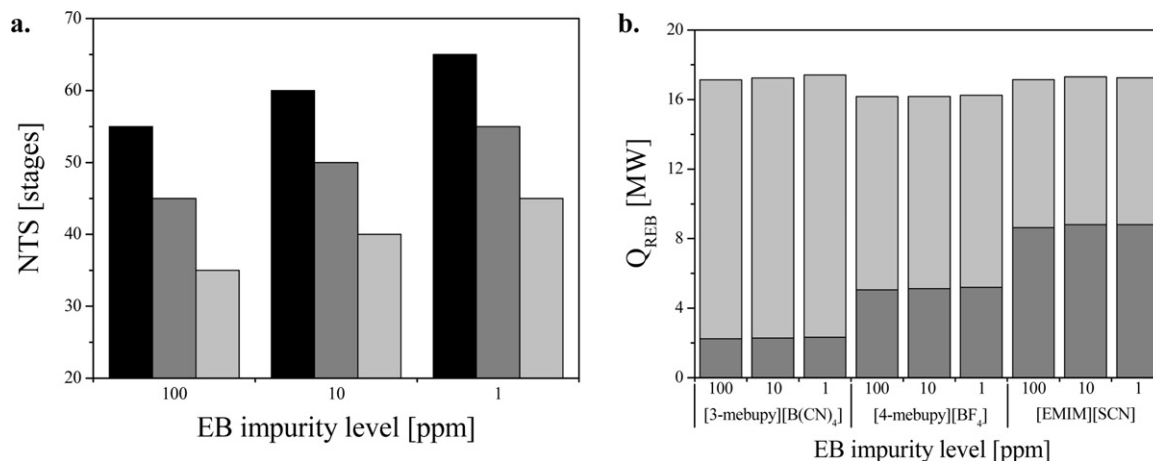


Fig. 9 – (a) Required number of stages (NTS) in the extractive distillation operations for the different ionic liquids and ethylbenzene impurity levels. Blacks bars, [3-mebupy][B(CN)₄]; grey bars, [4-mebupy][BF₄]; light grey bars, [EMIM][SCN]. (b) Required reboiler heat duty (Q_{REB}) for the different ILs and ethylbenzene impurity levels. Grey bars, solvent heating; light grey bars, evaporation.

lead to liquid–liquid phase splitting. This cannot be avoided when even more IL is recycled. The maximum allowable styrene concentrations in the IL recycles can be translated to the minimum IL purity, which needs to be at least 98.6, 99.6, and 99.76 wt%, respectively for the ILs [3-mebupy][B(CN)₄], [4-mebupy][BF₄], and [EMIM][SCN].

Subsequently, it was explored if these IL purities can be obtained using an evaporator which operates at mild conditions ($T=130^{\circ}\text{C}$, $P=11.1\text{ mbar}$, see Section 3). Using these conditions, IL purities of 99.0, 99.5, and 99.7 wt% can be obtained for the ILs [3-mebupy][B(CN)₄], [4-mebupy][BF₄], and

[EMIM][SCN], respectively. It follows that the IL purity constraint for the [3-mebupy][B(CN)₄] can easily be satisfied with an evaporator operating at mild conditions, but not for the other ILs. However, a large part of the styrene could already be recovered using an evaporator at mild conditions; 97% for [4-mebupy][BF₄] and 96% for [EMIM][SCN]. Hence, a second evaporator at lower pressures is required to further purify the ILs [4-mebupy][BF₄] and [EMIM][SCN]. Both ILs were regenerated to a purity of 99.9 wt%, because previous work on the IL regeneration showed that purifying the IL to a slightly higher purity than the minimum required purity, lowers the

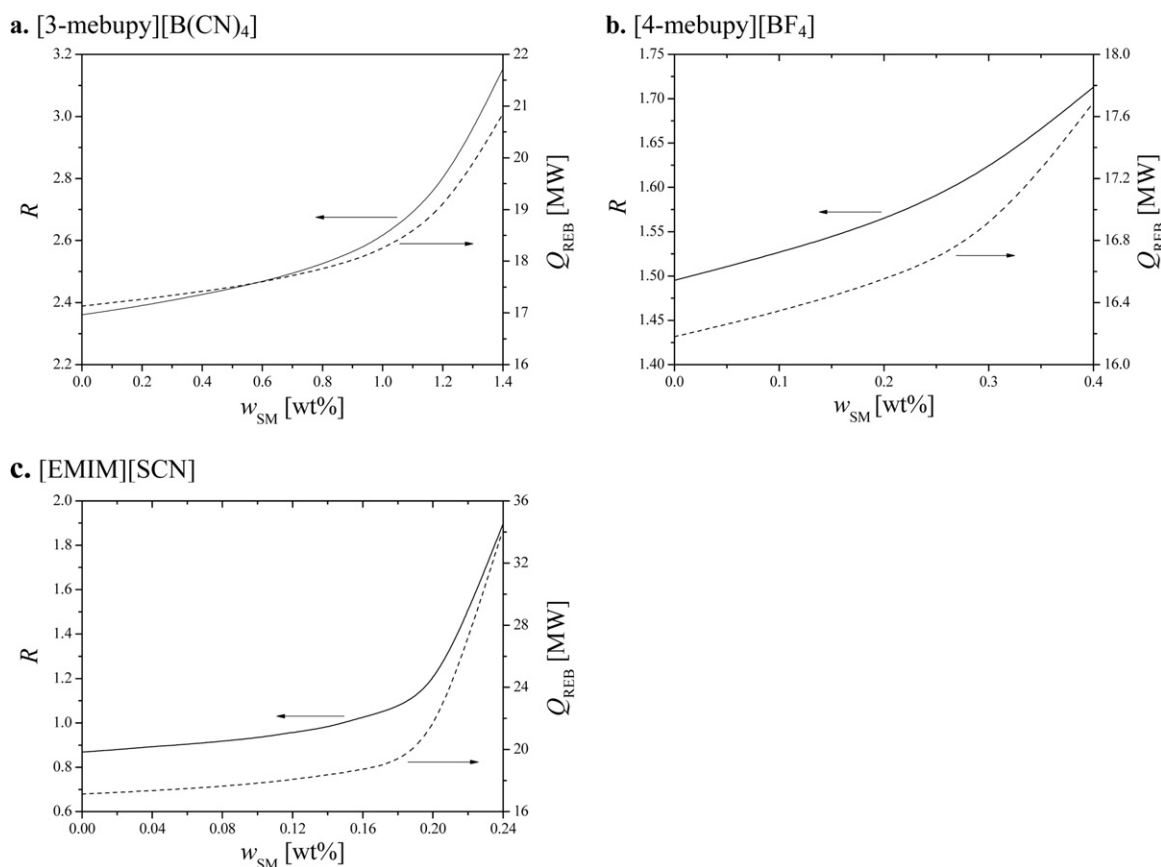


Fig. 10 – Influence of styrene mass concentration (w_{SM}) in the ionic liquid recycle on the reflux ratio (R) and reboiler heat duty (Q_{REB}) of the extractive distillation. (—) R ; (---) Q_{REB} . (a) [3-mebupy][B(CN)₄], (b) [4-mebupy][BF₄] and (c) [EMIM][SCN].

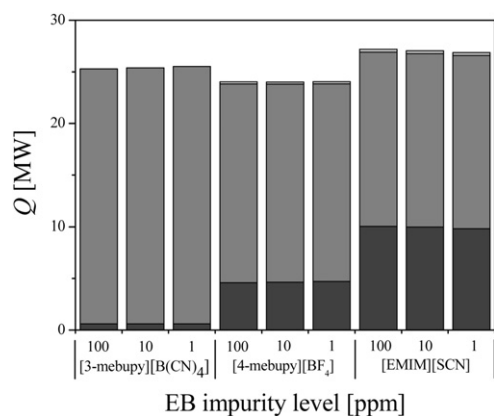


Fig. 11 – Total energy requirements extractive distillation processes for the different ILs and ethylbenzene impurity levels. Dark grey bars, solvent heating; grey bars, evaporation; light grey bars, refrigeration.

energy requirements in the reboiler of the extractive distillation (Jongmans et al., submitted for publication). Vacuum

pressures of 2.64 and 4.43 mbar were required for the ILs [4-mebupy][BF₄] and [EMIM][SCN], correspondingly.

4.3.3. Heat integration

Finally, the total extractive distillation process was modeled for the three ILs by closing the IL recycle and applying heat integration. The final process scheme for the IL [3-mebupy][B(CN)₄] is shown in Fig. 1c. The process diagrams for the ILs [4-mebupy][BF₄] and [EMIM][SCN] are depicted in Fig. 1d. It was not possible for the ILs [4-mebupy][BF₄] and [EMIM][SCN] to apply heat integration by evaporating part of the organic feed stream. The reflux ratio increases if part of the feed stream is evaporated. Thereby, the IL/organic ratio in the top of the column reduces, which causes liquid–liquid phase splitting. The total energy requirements are depicted in Fig. 11 for the different ILs. The total energy requirements are a summation of the energies required for solvent heating, evaporation, and refrigeration. The latter is required in the processes for the ILs [4-mebupy][BF₄] and [EMIM][SCN] to condense the evaporated styrene in the second evaporator. Fig. 11 shows that the extractive distillation process with [4-mebupy][BF₄] requires the lowest heat and cooling duties. However, there are no large differences in energy

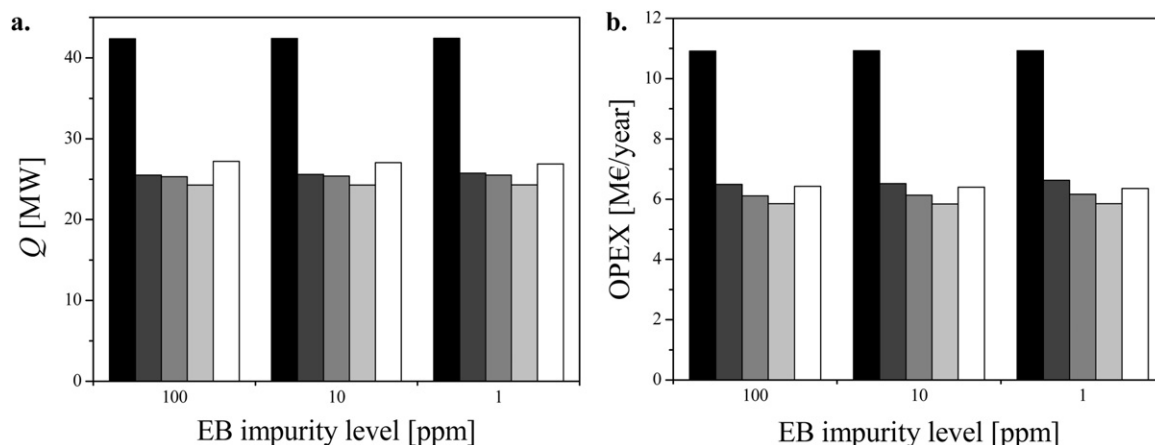


Fig. 12 – (a) Total energy requirements of the different processes for the different ethylbenzene impurity levels. (b) Operation expenditures (OPEX) of the different processes for the different ethylbenzene impurity levels. Black bars, distillation; Dark grey bars, sulfolane; grey bars, [3-mebupy][B(CN)₄]; light grey bars, [4-mebupy][BF₄]; white bars, [EMIM][SCN].

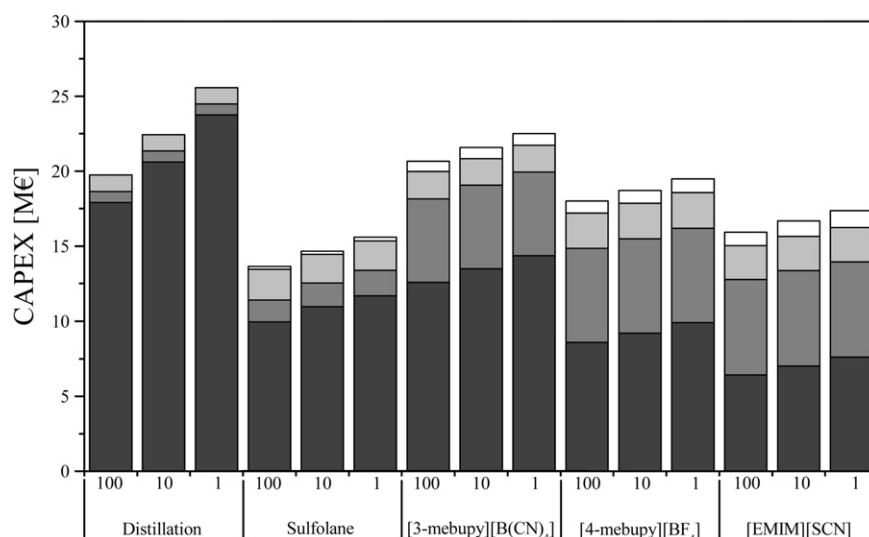


Fig. 13 – Capital expenditures (CAPEX) for the different processes and ethylbenzene impurity levels. Dark grey bars (extractive) distillation column; grey bars; solvent recovery unit; light grey bars, heat exchangers; white bars, solvent investment.

requirements between the extractive distillation processes for the different ILs. Therefore, the conclusion can be drawn that it does not make a big difference if an IL is selected with a high selectivity and low solvent capacity, or an IL with a low selectivity and a high solvent capacity. Fig. 11 shows also that still considerable energy duties are required for solvent heating despite the heat integration for the processes with the ILs [4-mebupy][BF₄] (19%) and [EMIM][SCN] (37.4%). For the IL [3-mebupy][B(CN)₄] only 2.4% of the total heat duty is required for solvent heating. This solvent heating is required in the extractive distillation column, which cannot be recovered by applying heat integration on the reboiler. Therefore, the energy requirements for solvent heating in Fig. 11 are also almost similar to the energy requirements for solvent heating presented in Fig. 9b. Fig. 11 also shows that there are no large differences in energy consumption between the different ethylbenzene impurity levels, which originates from the larger amount of stages selected for the lower ethylbenzene impurity levels. The different IL processes are compared to the sulfolane and the conventional distillation processes in the next section.

4.4. Overview all processes

The total energy requirements and OPEX are presented in Fig. 12 for all processes. From Fig. 12a, the conclusion can be drawn that all extractive distillation processes have lower energy requirements (40–45%) compared to the current distillation process. The extractive distillation processes using ILs do not outperform the extractive distillation process using sulfolane. Compared to the sulfolane extractive distillation processes the ILs [3-mebupy][B(CN)₄] and [4-mebupy][BF₄] save only ~1% and ~5%, respectively on the energy requirements, whereas the IL [EMIM][SCN] has ~5% higher energy requirements. The IL [4-mebupy][BF₄] slightly outperformed the other ILs. The process with [4-mebupy][BF₄] has 46.5% and ~10% lower OPEX compared to the distillation and sulfolane extractive distillation process, respectively, which is illustrated in Fig. 12b.

The CAPEX for the different processes are presented in Fig. 13. The CAPEX are a summation of the investment requirements for the (extractive) distillation column, solvent recovery unit, heat exchangers, and solvent investment. Fig. 13 shows that the largest investment is required for the (extractive) distillation column for all processes. This column is by far the largest equipment in size, and the costs for the structured packing Mellapak 250X contribute significantly to the total column investment (~50%). The IL processes require all a lower CAPEX than the current distillation process, except for the process with the IL [3-mebupy][B(CN)₄] at an ethylbenzene impurity level of 100 ppm. The sulfolane extractive distillation process clearly requires the lowest CAPEX. The large difference between the extractive distillation processes using ILs and sulfolane originates mainly from the difference in investment for the solvent recovery unit. The solvent recovery unit is the second largest contributor to the total CAPEX of the extractive distillation processes with the ILs. The forced circulating evaporator (~5.5 M€) and falling film evaporator (~0.9 M€) are both relatively expensive. The differences in CAPEX between the IL processes are dominated by the different investments for the extractive distillation column. The column investments are clearly the lowest for the IL [EMIM][SCN], because for this IL the lowest amount of stages (column height) is required and the lowest reflux ratio (column diameter). The solvent investment

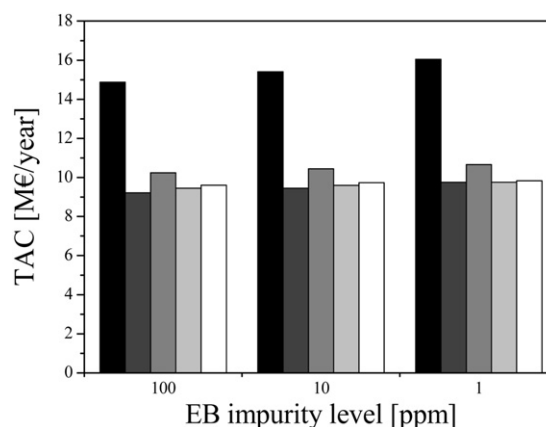


Fig. 14 – Total annual costs (TAC) for the different processes and ethylbenzene impurity levels. Black bars, distillation; dark grey bars, sulfolane; grey bars, [3-mebupy][B(CN)₄]; light grey bars, [4-mebupy][BF₄]; white bars, [EMIM][SCN].

contributes only 3–7%, depending on the IL, to the CAPEX of the extractive distillation processes at an IL price of 25 €/kg. At an IL price of 200 €/kg, the solvent investment would contribute about 23% to the total investment. Finally, the calculated TAC are depicted in Fig. 14. From this figure, the conclusion can be drawn that all extractive distillation processes have lower TAC than the current distillation process. However, sulfolane gives slightly lower TAC than the ILs. ILs can thus not outperform sulfolane to separate ethylbenzene from styrene by extractive distillation.

5. Conclusions

A conceptual design study was performed to investigate whether extractive distillation using ILs is a promising technology to separate the ethylbenzene/styrene mixture up to high styrene purities. Extractive distillation with sulfolane and the current distillation process were taken as the benchmark processes. Three ILs were studied: [3-mebupy][B(CN)₄], [4-mebupy][BF₄], and [EMIM][SCN]. The IL [4-mebupy][BF₄] slightly outperformed the other two ILs with up to 11.5% lower energy requirements. The operational expenditures of the [4-mebupy][BF₄] process are 43.2% lower than the current distillation process and 5% lower than extractive distillation with sulfolane. The capital expenditures were about 23% lower for the sulfolane process compared to the [4-mebupy][BF₄] process. Finally, from the total annual costs, the conclusion can be drawn that all extractive distillation processes outperform the current distillation process to obtain high purity styrene, but that ILs do not perform better than sulfolane.

References

- Al-Azzawi, S.F., Awwad, A.M., 1990. Excess molar volumes, excess logarithmic viscosities, and excess activation energies of viscous flow for 2-ethoxyethanol + γ -butyrolactone and +sulfolane at 303.15 K. *J. Chem. Eng. Data* 35, 411–414.
- Arenas, M.F., Reddy, R.G., 2003. Corrosion of steel in ionic liquids. *J. Min. Metall.* 39, 81–91.
- ASPEN Plus V7.2, User Guide. 1st ed., 2011.
- Bandres, I., Giner, B., Artigas, H., Royo, F.M., Lafuente, C., 2008. Thermophysical comparative study of two isomeric pyridinium-based ionic liquids. *J. Phys. Chem. B* 112, 3077–3084.

- Baur, R., Higler, A.P., Taylor, R., Krishna, R., 2000. Comparison of equilibrium stage and nonequilibrium stage models for reactive distillation. *Chem. Eng. J.* 76, 33–47.
- Beste, Y., Eggersmann, M., Schoenmakers, H., 2005. Extraktivdestillation mit ionischen Flüssigkeiten. *Chem. Eng. Technol.* 77, 1800–1808.
- Castagnolo, M., Inglese, A., Petrella, G., Sacco, A., 1981. Volumes and heat capacities of binary liquid mixtures of water–sulfolane and water–hexamethylphosphotriamide. *Thermochim. Acta* 44, 67–76.
- Chen, S., 2000. In: Seidel, A. (Ed.), *Kirk-Othmer Encyclopedia of Chemical Technology*. John Wiley & Sons, New Jersey.
- DIY Trade. <<http://www.diytrade.com/china/4/products/3196215/sulfolane.html>>, 2011.
- Doherty, M.F., Knapp, J.P., 2000. *Distillation, Azeotropic, and Extractive*. John Wiley & Sons, Inc.
- Domanska, U., Krolikowska, M., Krolikowski, M., 2010. Phase behaviour and physico-chemical properties of the binary systems {1-ethyl-3-methylimidazolium thiocyanate, or 1-ethyl-3-methylimidazolium tosylate + water, or + an alcohol}. *Fluid Phase Equilib.* 294, 72–83.
- Dutch Association of Cost Engineers, 2011. *DACE Prijzenboekje*, 28th ed. Reed Business, Doetinchem.
- Fenske, M.R., 1932. Fractionation of Straight-Run Pennsylvania Gasoline. *Ind. Eng. Chem.* 24, 482–485.
- Ficke, L.E., Novak, R.R., Brennecke, J.F., 2010. Thermodynamic and thermophysical properties of ionic liquid + water systems. *J. Chem. Eng. Data* 55, 4946–4950.
- Gentry, J.C., Kumar, S., Wright-Wytcherley, R., 2004. Use extractive distillation to simplify petrochemical processes. *Hydrocarb. Process.* 93, 62–66.
- Giernoth, R., 2010. Task-specific ionic liquids. *Angew. Chem. Int. Ed.* 49, 2834–2839.
- Gmehling, J., Onken, U., 1977. *Vapor–Liquid Equilibrium Data Collection*. DECHEMA, Frankfurt.
- Gomez, P., Gil, I., 2007. *Proceedings of European Congress of Chemical Engineering*, pp. 1–19.
- Hansmeier, A.R., Jongmans, M.T.G., Meindersma, G.W., de Haan, A.B., 2010. LLE data for the ionic liquid 3-methyl-N-butyl pyridinium dicyanamide with several aromatic and aliphatic hydrocarbons. *J. Chem. Thermodyn.* 42, 484–490.
- Hömmrich, U., Rautenbach, R., 1998. Design and optimization of combined pervaporation/distillation processes for the production of MTBE. *J. Membr. Sci.* 146, 53–64.
- Jongmans, M.T.G., Hermans, E., Schuur, B., de Haan, A.B., 2012a. Binary and ternary vapor–liquid equilibrium data of the system ethylbenzene + styrene + 3-methyl-N-butylpyridinium tetracyanoborate at vacuum conditions and liquid–liquid equilibrium data of their binary systems. *Fluid Phase Equilib.* 315, 99–106.
- Jongmans, M.T.G., Maassen, J.I.W., Luijks, A.J., Schuur, B., de Haan, A.B., 2011a. Isobaric low-pressure vapor–liquid equilibrium data for ethylbenzene + styrene + sulfolane and the three constituent binary systems. *J. Chem. Eng. Data* 56, 3510–3517.
- Jongmans, M.T.G., Raijmakers, M., Schuur, B., de Haan, A.B., 2012b. Binary and ternary vapor–liquid equilibrium data of the system (ethylbenzene + styrene + 4-methyl-N-butylpyridinium tetrafluoroborate) at vacuum conditions and liquid–liquid equilibrium data of their binary systems. *J. Chem. Eng. Data*, <http://dx.doi.org/10.1021/je201205t>.
- Jongmans, M.T.G., Schuur, B., de Haan, A.B., 2011b. Ionic liquid screening for ethylbenzene/styrene separation by extractive distillation. *Ind. Eng. Chem. Res.* 50, 10800–10810.
- Jongmans, M.T.G., Schuur, B., de Haan, A.B., 2012c. Binary and ternary LLE data of the system (ethylbenzene + styrene + 1-ethyl-3-methylimidazolium thiocyanate) and binary VLE data of the system (styrene + 1-ethyl-3-methylimidazolium thiocyanate). *J. Chem. Thermodyn.*
- Jongmans, M.T.G., Trampé, J., Schuur, B., de Haan, A.B. Styrene monomer recovery from ionic liquids. *Chem. Eng. Proc.*, submitted for publication.
- Jork, C., Kristen, C., Pieraccini, D., Stark, A., Chiappe, C., Beste, Y.A., Arlt, W., 2005. Tailor-made ionic liquids. *J. Chem. Thermodyn.* 37, 537–558.
- Kossack, S., Kraemer, K., Gani, R., Marquardt, W., 2008. A systematic synthesis framework for extractive distillation processes. *Chem. Eng. Res. Des.* 86, 781–792.
- Kyle, B.G., Leng, D.E., 1965. Solvent selection for extractive distillation. *Ind. Eng. Chem.* 57, 43–48.
- Lee, F.M., Gentry, J.C., 1997. Don't overlook extractive distillation. *Chem. Eng. Process.* 93, 56–64.
- Lei, Z., Arlt, W., Wasserscheid, P., 2007. Selection of entrainers in the 1-hexene/n-hexane system with a limited solubility. *Fluid Phase Equilib.* 260, 29–35.
- Lei, Z., Chen, B., Ding, Z., 2005. *Special Distillation Processes*. Elsevier, Amsterdam, pp. 59–144.
- Lide, D.R., Haynes, W.M., 2009. *Handbook of Chemistry and Physics*, 87th ed. Taylor and Francis group LLC, London.
- Marsh, K.N., Boxall, J.A., Lichtenthaler, R., 2004. Room temperature ionic liquids and their mixtures—a review. *Fluid Phase Equilib.* 219, 93–98.
- Meindersma, G.W., de Haan, A.B., 2008. Conceptual process design for aromatic/aliphatic separation with ionic liquids. *Chem. Eng. Res. Des.* 86, 745–752.
- Meindersma, G.W., Galan Sanchez, L.M., Hansmeier, A.R., de Haan, A.B., 2007. Application of task-specific ionic liquids for intensified separations. *Monatsh. Chem.* 138, 1125–1136.
- Meindersma, G.W., Simons, B.T.J., de Haan, A.B., 2011. Physical properties of 3-methyl-N-butylpyridinium tetracyanoborate and 1-butyl-1-methylpyrrolidinium tetracyanoborate and ternary LLE data of [3-mebupy]B(CN)₄ with an aromatic and an aliphatic hydrocarbon at T = 303.2 and 328.2 K and p = 0.1 MPA. *J. Chem. Thermodyn.* 43, 1628–1640.
- Onink, S.A.F., Aerts, G.H.F., Burghoff, B., Meindersma, G.W., de Haan, A.B. Ion chromatography as a novel method to quantify the solubility of ionic liquids in organic solvents. *J. Liq. Chromatogr.*, submitted for publication.
- Perry, R.H., Green, D.W., 1997. *Perry's Chemical Engineers Handbook*, 7th ed. McGraw-Hill, New York.
- Pinto, R.T.P., Wolf-Maciel, M.R., Lintomen, L., 2000. Saline extractive distillation process for ethanol purification. *Comput. Chem. Eng.* 24, 1689–1694.
- Poling, B.E., Prausnitz, J.M., O'Connell, J.P., 2007. *The Properties of Gases and Liquids*, 5th ed. McGraw Hill, Singapore.
- Renon, H., Prausnitz, J.M., 1968. Local compositions in thermodynamic excess functions for liquid mixtures. *AIChE J.* 14, 135–144.
- Richardson, J.F., Harker, J.H., Backhurst, J.R., 2002. *Coulson & Richardson's Chemical Engineering*, 5th ed. Butterworth Heinemann, Oxford.
- Sanchez, L.G., Espel, J.R., Onink, F., Meindersma, G.W., de Haan, A.B., 2009. Density, viscosity and surface tension of synthesis grade imidazolium, pyridinium, and pyrrolidinium based room temperature ionic liquids. *J. Chem. Eng. Data* 54, 2803–2812.
- Seider, W.D., Seader, J.D., Lewin, D.R., 2004. *Product & Process Design Principles*, 2nd ed. John Wiley & Sons, New York.
- Souders, M., 1964. The counter current separation process. *Chem. Eng. Prog.* 60, 75–82.
- Steltenpohl, P., Chlebovec, M., Graczoza, E., 2005. Simulation of toluene extractive distillation from a mixture with heptane. *Chem. Pap.* 59, 421–427.
- Stewart, O., Minnear, L., 2011. *Sulfolane Technical Assistance and Evaluation Report*. Oasis Environmental.
- Sucksmith, I., 1982. Extractive distillation saves energy. *Chem. Eng.* 89, 91–95.
- Uerdingen, M., Treber, C., Balsler, M., Schmitt, G., Werner, C., 2005. Corrosion behaviour of ionic liquids. *Green Chem.* 7, 321–325.
- Underwood, A.J.V., 1932. The theory and practice of testing skills. *Trans. Am. Inst. Chem. Eng.* 10, 112.
- Ward, A.L., Robert, W.J., 2000. In: Arza Seidel (Ed.), *Kirk-Othmer Encyclopedia of Chemical Technology*. John Wiley & Sons, New York.

Wasserscheid, P., Welton, T., 2008. In: Wasserscheid, P., Welton, T. (Eds.), *Ionic Liquids in Synthesis*. Wiley-VCH, Weinheim, pp. 1–6.

Welch, V.A., 2001. US 6171449 B1.

Yin, W., Ding, S., Xia, S., Ma, P., Huang, X., Zhu, Z., 2010. Cosolvent selection for benzene cyclohexane separation in extractive distillation. *J. Chem. Eng. Data* 55, 3274–3277.