

Thiophene extraction from n-heptane and n-octane using ionic liquids

An insight into the desulfurization of fuels





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Abstract

The viability of the removal of thiophene from an n-heptane/n-octane mixture using extraction with ionic liquids, as a replacement of sulfolane, is explored in this master thesis. The mixture is a simple model for fuel desulfurization, with the goal to reduce the thiophene content to 10 ppm, from 520 ppm. The ionic liquids, [EMIM][MeSO₃] and [EIM][NO₃] are chosen using an extensive Matlab screening program, which employs infinite dilution activity coefficients. Subsequent experimental work obtained liquid-liquid equilibria data, which were used to regress NRTL parameters. With the NRTL values, as well as other property data, both theoretical process design and process design in Aspen Plus was done. Other property data includes viscosity, surface tension, heat capacity, thermal conductivity, critical properties, acentric factor and density. Using the results of this design it was concluded that, although [EMIM][MeSO₃] has better extractive properties, [EIM][NO₃] is the better option for this particular process. This is mostly due to its lower boiling point, greatly reducing utility costs. Moreover, it was concluded that both ionic liquids were a suitable replacement for sulfolane.

Preface

I would like to use this opportunity at the start of this thesis to express my utmost gratitude towards several people. Firstly, Daili Peng, for his extensive help throughout the project. Without his extensive knowledge of ionic liquids, it would not have been possible. Secondly, Léon Rohrbach, for his tremendous amount of help and insight for the experimental section of this work. Lastly, Balaji Sridharan, for his help on the use of Aspen Plus. I could not have done it without the three of you, thank you.

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Nomenclature list

Latin letters

- a: specific surface area
- (A)RDC: (asymmetric) rotating disc contactor
- C7: n-heptane
- C8: n-octane
- C9: n-nonane
- d₃₂: Sauter mean diameter
- D: diameter
- e: fraction free cross-sectional area
- E: axial dispersion coefficient
- E_{fr}: lost frictional energy
- EC₅₀: half maximal effective concentration
- f_i: fugacity of pure species
- $\bar{f_i}$: fugacity of species in solution
- f: Fanning's friction factor in mechanical energy balance
- g: gravitational constant
- G: Gibbs free energy
- H_c: tray height
- K_W: friction loss factor
- LD₅₀: median lethal dose
- M_z: magnetization of a compound
- Mlb: 1000 pounds
- N: rotational speed of rotor
- N_T =number of stages
- N_{Tubes}: number of tubes in a heat exchanger
- OF: objective function
- P: power
- PI: performance index
- R: gas constant
- RRF: relative response factor

- S: selectivity
- t: time
- T: temperature
- Thio: Thiophene (in some experimental results)
- u: true velocity of phase
- U: superficial velocity of phase
- U: Overall heat transfer coefficient (W/m².K)
- w: weight fraction
- x: molar fraction

Greek alphabet

- $\boldsymbol{\alpha}:$ non-randomness parameter, one of the constants used in NRTL
- β : distribution coefficient
- ΔT_m : logarithmic mean temperature difference
- γ : activity coefficient
- $\gamma_{i,T}$: interfacial tension
- ϵ : power dissipation per unit mass
- ϵ : void fraction
- η: viscosity
- μ: internal energy
- ρ: density
- $\tau :$ one of the constants used in NRTL
- τ : residence time of the column
- ϕ : volume fraction/hold-up
- $\varphi_{\mathbb{A}}$: the amount of energy added to the system in mechanical energy balance
- ϕ_m : volumetric flowrate
- φ_V : volumetric flowrate
- ω : liquid-liquid splitting ratio (in NRTL calculations)
- ω : acentric factor (in properties)

Sub- and superscript

C: column

- c: continuous phase
- cr: critical

d: dispersed phase E: excess f: flood point H: heavy component/phase HC: hydrocarbon (layer) hyd: hydraulic, as in hydraulic diameter IL: lonic Liquid (layer) id: ideal L: light component/phase R: rotor shaft: rotating shaft of the rdc S: stator ring in RDC

 α : alpha phase (in internal energy)

- β: beta phase (in internal energy)
- ∞ : at infinite dilution
- 0: at standard conditions, at 0
- 1: the ionic liquid
- 2: thiophene
- 3: n-heptane or n-octane

Introduction

Aim of this thesis

This thesis aims to find suitable ionic liquids for the extraction of thiophene from n-heptane and noctane, to mimic an important desulfurization process for gasoline. The decision of this system is explored in a later section and based on Matlab screening using infinite dilution activity coefficients. After a suitable ionic liquid is chosen, experimental work is done. In the experimental work, the liquidliquid equilibria (LLE) is determined for the ionic liquid (1), thiophene (2) and n-heptane or n-octane (3) systems. This LLE data is regressed to NRTL constants for implementation into Aspen Plus, where process design is performed. The process design consisted of an extraction and ionic liquid recovery step. In the end, conclusions were drawn as to which ionic liquid is the better option of the two as well as the general applicability of the extraction process.

A list of used symbols can be found before the introduction. An overview of all used figures, tables and equations is depicted in appendix K at the very end of this thesis.

Ionic liquids

lonic liquids (IL) consist of an anion and a cation, as the name suggests. Moreover, they are liquid at their applied temperature, mostly around room temperature (Welton, 2018). Due to the vast number of available of anions and cations a plethora of different ionic liquids exist. An overview of different common cations is given in Figure 1, with the x denoting substituted chains, such as alkyls, hydroxyl groups, protons, ethers, fluors, benzyls and allyls (Lazzús & Pulgar-Villarroel, 2015). Due to this large variety of side chains available, the number of different cations is enormous. Furthermore, a large number of different anions is available with a lot of them being denoted in the works of Lazzús et al. These anions include, but are not limited to, sulphides, halogens, metal halogen complexes, phosphors, cyanide compounds, fluoride complexes and more (Lazzús & Pulgar-Villarroel, 2015).



Figure 1 Different cations available (Lazzús & Pulgar-Villarroel, 2015)

ILs were first discovered by Paul Walden when he was searching for a molten salt which was liquid at room temperature, an important characteristic of many ionic liquids. He accomplished this in 1914 when he discovered that [EtNH₃][NO₃] has a melting point of 12°C (Welton, 2018). After this there was not much interest in ionic liquids for a long time, until the fifties of the last century when another group started working on them within the field of electrochemistry (Hurley & Wier, 1951), which remained an important field for ionic liquids. Over the last 69 years, the field of ionic liquids has been developed further. The use cases for ionic liquids are various, with reports of it being using for green energy (Kowsari, 2016), pharmaceuticals, extractions, catalysts, electrochemical purposes and solvents

(Brooks, 2014). This work focuses on its applications for extractive purposes. Specifically, the extraction of thiophene from fuel oil, which is modelled as n-heptane and n-octane.

Thiophene

Thiophene is a major part of crude oil, where it is responsible for a large part of the H₂S present in the hydrodesulphurization process in oil refineries, together with elemental sulphur, mercaptans and (di)sulphides (Rychlewska, Konieczny, & Bodzek, 2015). The H₂S is created by the hydrotreating process, which turns, amongst others, nitrogen and sulphur impurities into NH₃ and H₂S respectively, in the presence of a catalyst and hydrogen (Fahim, Alsahhaf, & Elkilani, 2010). The conversion of thiophene is depicted in Reaction equation 1. This reaction is highly exothermic (Δ H=-284.2 kJ/mol), but it is run at a high temperature to promote the reaction kinetics, i.e. 395°C at 15 bar for 99% conversion of thiophene (Fahim et al., 2010). After the hydrotreating, the H₂S is removed using amine scrubbing and the butane is removed from the heavier fraction (Fahim et al., 2010).



Reaction equation 1 thiophene hydrotreating (Fahim et al., 2010)



Figure 2 Thiophene

Sulfolane process

The process that ionic liquids aim to replace, is the extraction process using sulfolane, see Figure 3, which is the current commercially available extraction process for aromatics from petroleum (Hansmeier, Meindersma, & de Haan, 2011). It has been reported that sulfolane is able to remove both sulphur and nitrogen compounds from gas oil (S. Kumar, Srivastava, Nanoti, & Kumar, 2015). (Song, Zhang, Qi, Zhou, & Sundmacher, 2018) analysed a process where thiophene is extracted from an n-octane, cyclohexane and thiophene mixture using both a variety of ionic liquids and sulfolane. As can be seen from the structure of sulfolane, it is also soluble in the oil phase. Therefore it requires two purification steps, for both the top and bottom stream of the extraction process, see Figure 4 (Song et al., 2018). Because the sulfolane process requires two distillation towers, whereas the ionic liquid process only requires one, as is shown later, ionic liquids have the potential to greatly reduce the energy required for extraction. The process conditions of (Song et al., 2018) are shown in Table 1, which are used in the comparison between the ionic liquids and sulfolane.

Lastly, it should be added that the LD_{50} , the median lethal dose, of sulfolane is 1800 mg/kg body weight and at lower concentrations, it qualifies as a neurotoxin (Dinh, Hakimabadi, & Pham, 2020). This is particularly problematic due to the bad biodegradability and high mobility of sulfolane leaks (Dinh et al., 2020). It is important that the environmental impact, in terms of toxicity, is lower for the ionic liquid that aims to replace sulfolane.



Figure 3 Sulfolane



Figure 4 The extraction process of thiophene from fuels, using Sulfolane (Song et al., 2018)

Table 1 Process conditions of the thiophene extraction process designed by (Song et al., 2018) as shown in Figure 4.

Process condition	Results
Model fuel feed	10000 kg/h
Sulfolane make-up (S1)	2.76 kg/h
Sulfolane in recycle (S7 and S9)	13341.3 kg/h
Number of stages distillation column	10 (both)
Heat duty	1709.19 kW (B2)
Heat duty	4172.58 kW (B3)

Liquid-liquid equilibria: A thermodynamical background

Systems with multiple phases at the same temperature and pressure are in equilibrium when the chemical potential for each component is equal to each other in both phases (J. . Smith, Van Ness, & Abbott, 2005a). The chemical potential of a species in solution is denoted in Equation 1, with Γ being an integration constant at constant T and $\bar{f_i}$ the fugacity of a species in solution (J. . Smith et al., 2005a). Because the temperature is equal for both phases it can be deduced that the fugacities of the species in both phases need to be equal to each other.

$$\mu_i^{\alpha} = \mu_i^{\beta}$$
$$\mu_i \equiv \bar{G}_i = \Gamma_i(T) + RT ln(\bar{f}_i)$$
$$\bar{f}_i^{\alpha} = \bar{f}_i^{\beta}$$

Equation 1 internal energy of a species related to the fugacity in solution of the component. (J. . Smith et al., 2005a)

The principle of LLE relies on the fugacity of both species being equal to each other in both phases (Nevers, 2012). Using Raoult's law with activity coefficient, this can be rewritten using the mole fraction x, the activity coefficient γ and the vapour pressure p, see Equation 2 (Nevers, 2012). Because the vapour pressure of a component is equal for both phases, these can be removed from the equation. Note, that this does not strictly apply to an ionic liquid component, because of the hydrocarbon layer being devoid of ionic liquid, making Equation 2 read $0=x_1^{1L}\gamma_1^{1L}$, which is not the case.

$$f_i^{HC} = f_i^{IL} \rightarrow x_i^{HC} \gamma_i^{HC} p_i^{HC} = x_i^{IL} \gamma_i^{IL} p_i^{IL} \rightarrow x_i^{HC} \gamma_i^{HC} = x_i^{IL} \gamma_i^{IL}$$

Equation 2 fugacity rewritten with Raoult's law with activity coefficients for a two-phase system (Nevers, 2012)

Where the approach with Raoult's law assumes an ideal state for the liquid, another approach might also be suitable, which assumes there is an excess property, which is the difference between the actual value of the property and the value if it behaved ideally (J. . Smith et al., 2005a). In this work, the relation between the actual and ideal property, the focus is on the fugacity of a species in solution, i.e. $\bar{f_i}$, and the fugacity for the ideal case, i.e. $x_i f_i$. N.B. the lack of the bar signifies that it is the fugacity of pure species i (J. . Smith et al., 2005a). Using the middle formula of Equation 1 the following derivation is obtained, see Equation 3. In the last line the dimensionless relation $\bar{f_i}/x_i f_i$ is replaced by the activity coefficient, which is by definition (J. . Smith et al., 2005a). Furthermore, for an ideal mixture, the excess Gibbs energy is zero and therefore activity coefficient is equal to 1. Lastly, by using the relation between chemical potential, Gibbs free energy and the mole fraction of i in the liquid, a formula can be created that describes the chemical potential in a non-ideal system, given in Equation 4 (J. . Smith et al., 2005a).

$$\bar{G}_{i}^{E} = \bar{G}_{i} - \bar{G}_{i}^{id}$$
$$\bar{G}_{i} = \Gamma_{i}(T) + RTln(\bar{f}_{i})$$
$$\bar{G}_{i}^{id} = \Gamma_{i}(T) + RTln(x_{i}f_{i})$$
$$\bar{G}_{i}^{E} = RTln\left(\frac{\bar{f}_{i}}{x_{i}f_{i}}\right)$$
$$\bar{G}_{i}^{E} = \bar{G}_{i} - \bar{G}_{i}^{id} = RTln(\gamma_{i})$$

Equation 3 excess Gibbs free energy for species i in solution (J. . Smith et al., 2005a)

$$\mu_i^{id} = G_i + RTln(x_i)$$
$$\mu_i = G_i + RTln(x_i\gamma_i)$$

Equation 4 chemical potential for a component i in a non-ideal solution (J. . Smith et al., 2005a)

When comparing both these approaches, one with Raoult's law and one with excess property, it can be concluded that the relation given in Equation 2 is true. Furthermore, one can also relate Equation 1 and the definition of the activity coefficient to each other and obtain Equation 5. Because all the

species exist as a liquid at the conditions of the system, the fugacity can be removed from the equation and Equation 2 is again obtained (J. . Smith, Van Ness, & Abbott, 2005b).

$$(x_i \gamma_i f_i)^{\alpha} = (x_i \gamma_i f_i)^{\beta}$$

Equation 5 LLE relation using fugacity (J. . Smith et al., 2005b)

Using the LLE data it is possible to calculate the selectivity (S) and distribution coefficient (β) using Equation 6 and Equation 7, with x being the mole fraction, index 1 is ionic liquid, 2 is the solute, which is thiophene in this work, 3 is the hydrocarbon solvent, which is n-heptane or n-octane, x^{HC} is the mole fraction in the hydrocarbon phase and x^{IL} is the mole fraction in the ionic liquid phase (Domańska, Lukoshko, & Królikowski, 2013). The selectivity is a measurement for effectiveness and is defined as the ratio of solubilities between the hydrocarbon and ionic liquid layer (Kroon & Peters, 2010), or as (Sinnott & Towler, 2013f) describe it: The ratio between the two distribution coefficients, in a system with two solutes and solvents. The distribution coefficient is defined as the ratio of mole fractions of the solute, in the two different layers (Nevers, 2012).

$$S = \frac{x_2^{HC} x_3^{IL}}{x_2^{IL} x_3^{HC}}$$

Equation 6 selectivity calculated with the mole fractions of thiophene and n-heptane/n-octane in the ionic liquid layer and hydrocarbon layer (Domańska et al., 2013; Larriba, Navarro, García, & Rodríguez, 2014)

$$\beta = \frac{x_2^{IL}}{x_2^{HC}}$$

Equation 7 distribution coefficient calculated with the mole fraction of thiophene in the ionic liquid layer and hydrocarbon layer (Domańska et al., 2013; Larriba et al., 2014)

Furthermore, the LLE can also be depicted in a so-called equilateral triangular diagram (or ternary plot). The triangle is filled with tie-lines obtained from two data points, where the data points on the left are obtained from the HC layer and on the right from the ionic liquid layer. An example is given in Figure 5. Because no ionic liquid should be present in the HC layer, the left-hand side points should all be on the same line. This means that only one binodal curve can be created (on the right), consequently, there is no plait point visible in the graph (Nevers, 2012). The region covered by the tie-lines is the so-called two-phase region (Nevers, 2012). Outside of the tie-lines, which only exists on a small strip on the right, a one-phase region is present. This only occurs at very high ionic liquid concentrations in the case of the thiophene, n-heptane and $[COC_2mMOR][FAP]$ mixture, shown in Figure 5.



Figure 5 equilateral triangular diagram for thiophene, n-heptane and [COC₂mMOR][FAP] system (Marciniak & Królikowski, 2012)

Matlab screening

Due to the large number of ionic liquids available a screening method was employed to obtain a suitable ionic liquid for an extraction process. For the calculations for the ionic liquid screening the infinite dilution activity coefficient (IDAC or γ^{∞}) is required, in relation to the ionic liquid, i.e. γ^{∞}_{1i} is molecule 'i' in the ionic liquid (1). The IDAC is the activity coefficient when a molecule is surrounded by a solvent, in this thesis' case the ionic liquid (Gruber, Langenheim, Gmehling, & Moollan, 1997). A list of IDACs for different ionic liquids with different components up to 2018 was provided and expanded to include papers from 2019. These papers generally contained a list of IDACs for different hydrocarbons in combination with a couple of ionic liquids and at set temperatures. Approximately 50000 combinations are considered.

Because the infinite dilution is only used for the screening of different ionic liquids, and the IDACs are only used with ionic liquid (1) as the solvent, i.e. γ_{12}^{∞} and γ_{13}^{∞} , a simplification can be made. For simplification let us assume a binary system, with two phases α and β . Species 2 is very dilute in phase α and 3 is very dilute in β , meaning that species 2 is the solvent of phase β and 3 is the solvent of α . For this system, the following is true (J. . Smith et al., 2005b):

$$\gamma_2^{\alpha} \approx \gamma_2^{\infty}$$
, $\gamma_3^{\alpha} \approx 1$, $\gamma_2^{\beta} \approx 1$, $\gamma_3^{\beta} \approx \gamma_3^{\infty}$

Now using Equation 5, without the fugacity, because it is equal for both phases, the following derivation can be obtained, to rewrite Equation 7 and Equation 6. See below, Equation 8.

$$x_{2}^{\alpha}\gamma_{2}^{\alpha} = x_{2}^{\beta}\gamma_{2}^{\beta} = x_{2}^{\beta}$$
$$\frac{x_{2}^{\alpha}}{x_{2}^{\beta}} = \frac{1}{\gamma_{2}^{\alpha}}$$
$$\beta_{2}^{\infty} = \frac{1}{\gamma_{2}^{\infty}}$$
$$S^{\infty} = \frac{\beta_{2}^{\infty}}{\beta_{3}^{\infty}} = \frac{\gamma_{3}^{\infty}}{\gamma_{2}^{\infty}}$$

Equation 8 derivation of the distribution and selectivity using infinite dilution activity coefficients

Using the vast database of IDACs the distribution coefficient, selectivity and performance index at infinite dilution can be calculated according to Equation 9 to Equation 11 (Peng, Zhang, Cheng, Chen, & Qi, 2017). The distribution coefficient is the amount of solute in the ionic liquid-rich phase (Ramalingam & Banerjee, 2011) and can be used synonymously with the word capacity, which is more frequently used in papers regarding the screening process (Kroon & Peters, 2010; Peng et al., 2017). By multiplying the distribution coefficient and selectivity at infinite dilution the performance index was obtained (Peng et al., 2017). Using this value, the best ionic liquids were selected, in term of extractive performance.

Using Matlab the different combinations of cations and anions for two set hydrocarbons to be separated, were analysed at a set temperature range. The Matlab code was obtained from Daili Peng but was modified to allow for IDACs at a temperature +/- 1K to be considered equal to the set temperature, see appendix A. Moreover, the code also filtered out ionic liquids that had a too high viscosity (>0.150 Pa.s). Two systems were considered: thiophene/n-heptane and thiophene/n-octane. For these systems, the best ionic liquids were selected and checked for available LLE data. The selected ionic are depicted in Table 12 and Table 13 respectively, which can be found in appendix A. Note that

[EMIM][MeSO₃] is in Table 13 twice because it had two different sources. Furthermore, the data is available at different temperatures due to the IDACs being available at different temperatures.

$$\beta^{\infty} = \frac{1}{\gamma_{12}^{\infty}}$$

Equation 9 distribution coefficient at infinite dilution for thiophene in the ionic liquid phase (Peng et al., 2017)

$$S^{\infty} = \frac{\gamma_{13}^{\infty}}{\gamma_{12}^{\infty}}$$

Equation 10 selectivity at infinite dilution (Peng et al., 2017)

$$PI^{\infty} = \beta^{\infty} \times S^{\infty}$$

Equation 11 performance index at infinite dilution (Peng et al., 2017)

It was decided to determine the LLE data for two different ionic liquids for both mixtures. Firstly, 1ethyl-3-methylimidazolium methanesulfonate [EMIM][MeSO₃], see Figure 6, because of its high PI, no LLE available and because it is liquid at room temperature. Secondly, because 1-ethyl-3methylimidazolium nitrate [EMIM][NO₃] is not liquid at room temperature, it was decided to do the experiment with a similar ionic liquid, which is not present in the database, namely ethylimidazolium nitrate [EIM][NO₃], see Figure 7. Both ionic liquids were obtained from IoLiTec, with the properties shown in appendix E. The goal of the LLE data is to obtain the selectivity and distribution coefficient and compare them to known LLE data, depicted in Figure 9 and Figure 10 for thiophene/n-heptane, and Figure 11 and Figure 12 for thiophene/n-octane (all four figures are shown in the results section), for which far less data is available. The experimental results are also shown in these graphs, as well as the two ionic liquids not chosen for this thesis, [DMIM][MP] and [BMIM][SCN], due to available LLE data.



Figure 6 1-ethyl-3-methylimidazolium methanesulfonate [EMIM][MeSO₃]



Figure 7 ethylimidazolium nitrate [EIM][NO₃]

Toxicity

The toxicity is measured using the half-maximal effective concentration, EC_{50} in μ M, or the often-used $log_{10}(EC_{50})$ (Cao, Zhu, Zhao, & Zhao, 2018). (Fatemi & Izadiyan, 2011) created multiple models for the determination of the cytotoxicity of ionic liquids. The models were based on quantitative structure-activity relationships (QSAR) (Fatemi & Izadiyan, 2011). From their research, they determined that the toxicity is mainly attributed to the cation, with the anion playing a secondary role (Fatemi & Izadiyan, 2011). The toxicity for [EMIM][MeSO₃] is very low, with a modelled $log_{10}(EC_{50})$ value between 3.57 and 3.97 (Fatemi & Izadiyan, 2011), an experimental value of 3.97 according to (Cao et al., 2018) or 4.0793

according to the prediction technique of (Peng & Picchioni, 2020) (higher is less toxic). (Peng & Picchioni, 2020) report a toxicity 4.3365 for [EIM][NO₃]. For comparative reasons, the ecotoxicity of sulfolane and thiophene are 500 mg/L or $log_{10}(EC_{50})=3.62$ and 21 mg/L or $log_{10}(EC_{50})=5.41$ (European Chemicals Agency, n.d.-a, n.d.-b), respectively. This means that sulfolane is more toxic than the chosen ionic liquids and thiophene is far less toxic.

The toxicity of $[EIM][NO_3]$ was also calculated using a model provided by (Luis, Ortiz, Aldaco, & Irabien, 2007), see Equation 12 and Equation 13. In this model the a, c and s are contributions for the anion, cation and side group respectively, the A, C and S determine if a certain group is present or not, by giving it either a 1 or a 0 (Luis et al., 2007). Using this method, the Y^{*} value of $[EIM][NO_3]$ was calculated to be 0.417 and consequently, $log_{10}(EC_{50})$ to be 2.70. This would mean that $[EIM][NO_3]$ is more toxic than $[EMIM][MeSO_3]$, which is unexpected because (Luis et al., 2007) reports that by increasing the alkyl chain on the alkylmethylimidazolium, the toxicity is also increased by 11% per extra carbon atom, and an extra methyl group, for example on the N+ atom, increases the toxicity by 7% (Luis et al., 2007). When calculating the Y^{*} of $[EMIM][MeSO_3]$ a value of 0.484 is obtained and a $log_{10}(EC_{50})$ of 2.36, which is significantly lower than the value reported by (Fatemi & Izadiyan, 2011), and would suggest it is far more toxic. However, (Luis et al., 2007) reports a decrease in toxicity for methylsulfate anion, but reports nothing for methanesulfonate.

$$Y^* = \sum_i a_i \cdot A_i + \sum_j c_j \cdot C_j + \sum_j s_k \cdot S_k$$

Equation 12 group contribution calculation for toxicity (1) (Luis et al., 2007)

 $\log_{10}(EC_{50}(\mu M)) = 4.76 - 4.94 Y^*$

Equation 13 group contribution calculation for toxicity (2) (Luis et al., 2007)

Scientific relevance

The high energetic requirement and subsequent environmental impact, for the hydrotreating process, looks to be a major downside. Ionic liquid extraction can prove to be beneficial to reduce energy usage in the petrol industry (Song et al., 2018). Furthermore, when an extractive process using sulfolane is used, two distillation towers are required, instead of the one that is required when ionic liquids are used, which gives validity to find a replacement for sulfolane (Song et al., 2018). Moreover, it has been shown that sulfolane is more toxic than the discussed ionic liquids, which poses a major environmental concern. There is a scientific necessity for finding a good replacement for sulfolane and this thesis explores the use of two ionic liquids for this task.

Experimental

The shaking method

This section entails the experimental method of determining the liquid-liquid equilibrium data (LLE) for the [EMIM][MeSO₃] or [EIM][NO₃], thiophene, n-heptane or n-octane systems (four systems in total). After several failed attempt using stirring at 500 RPM, it was decided to use a shaking method (200 strokes per minute SPM), similar to (Ramalingam & Balaji, 2015).

The ionic liquids were dried for two consecutive nights at 80°C and under vacuum. The bottles were equipped with tight-fitting septums, flushed with argon, and wrapped in parafilm. The ionic liquids were stored in a desiccator, with freshly dried silica. The day after, the water content was measured using coulometric Karl Fischer titration, in duplo. [EMIM][MeSO₃] had a water content of 484 to 2567 ppm (=0.25%) and [EIM][NO₃] a water content of 1900 to 795 ppm, before opening the bottle and after

drying, respectively. The water content of the ionic liquids before drying were provided via personal contact with the supplier, IoLiTec. The water increase in [EMIM][MeSO₃] could be due to the significant use, without a septum, before the drying, meaning that after opening the bottle and before drying, it was even higher than 2567 ppm, due to the attracted water. The Karl Fischer titration apparatus was tested using a hydranal sample with a known water content of 100 ppm, which resulted in a water content of 99.3 ppm according to the apparatus, which is a good result.

It was later decided to further dry the ionic liquids, for three days at 80°C under vacuum. After drying the bottles were fitted with new septums, wrapped in parafilm, and flushed with argon. The water content was again tested with coulometric Karl Fisher titration, in duplo. The following water contents were obtained: 3613 ppm for [EMIM][MeSO₃] and 781.7 for [EIM][NO₃]. This shows the difficulty that is present in drying these ionic liquids, in particular the former, which got even wetter since its last measurement. The mass fractions of water correspond to 0.025% and 0.00089% for [EMIM][MeSO₃] and [EIM][NO₃], respectively, i.e. the amount of water in the ionic liquid is negligible.

The samples were prepared in capped scintillation vials, wrapped in parafilm. All samples contain 50 wt% of ionic liquid, 5 to 30 wt% (in increments of 5 wt%) of thiophene and the rest (45 to 20 wt%) was either n-heptane or n-octane. This means that six experiments were performed for each system, so 24 experiments in total. The target was to fill the vials with approximately 4 g, however, due to the difficulty of dropping the ionic liquid and thiophene, all vials contain more or less than 4 g. For all systems, the weight percentages were correctly measured, using a Mettler analytical balance with a readability of 0.1 mg. The night before the experiment the vials were prepared with this method: first, the ionic liquid was added using a syringe through the septum of the ionic liquid vial. Secondly, the thiophene was added, using a pipette. Thirdly, the n-heptane or n-octane was added using a pipette. After all components were added the mass fractions were calculated and chemicals were added accordingly. Lastly, the vial was wrapped in parafilm and marked. One system was measured each time, meaning six experiments.

The next day the vials were put in a shaking machine and the vials were shaken for six hours at 200 strokes per minute. The shaking machine had no working climate control, however, the temperature in the lab was approximately 23 to 25°C. After the six hours, the vials were put in a water bath to settle overnight. To check if equilibrium was reached, one experiment (15 wt% thiophene, [EIM][NO₃] and n-heptane) was repeated and shaken for 16 hours. The results only differed a few per cents, confirming that equilibrium is reached before 6 hours of shaking. The water bath has a controlled temperature using another water bath, which pumped water through a cooling/heating element in the first water bath. The second water bath was a the Julabo F25-ED cooling and heater circulator, which has a temperature range of -20 to 100°C and a stability of 0.03°C. The water bath pumping the water had the ability to cool and heat water and was put on a constant 26°C because approximately 1°C was lost in the hose containing the pumped water. The water in the first water bath was kept at a constant 25°C. The temperature in the lab dropped to 22 to 24°C at night.

After settling, two layers had formed in the vials. The layers were separated into separate vials. The top layer was measured using low thermal mass gas chromatography (LTM-GC), with the method explained in the next section. The top layer was also analysed with H-NMR to check if any ionic liquid was present, which has not been the case. The bottom layer was measured using both 300 and 600 MHz H-NMR, depending on availability of the machine. Each system has the same machine used for all six vials. For all H-NMR samples, deuterated methanol (MeOD) was used as a solvent.

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Gas chromatography and internal standard.

For the GC the following settings were used:

- GC: Agilent Technologies 7890B
- Detector: FID 300°C
- Injector: Split/splitless
- Injector Temperature: 280°C
- Injection volume: 1 μL
- Split ratio: 1:100
- Column flow: 3 mL/min
- Oven temperature program: 40°C-0min-50°C/min-280°C-1min
- Column: Agilent Technologies DB-5 15m×0.32mm×0.25μm
- Interface temperature: 280°C

The amount of top layer in the GC vial (a few drops) was weighed. The GC samples also contained approximately 1.1 g of stock solution, which had an internal standard fitted to it. The stock solution contained approximately 99% of n-heptane or n-octane and 1% of n-nonane. The relative response factor was calculated using five known thiophene/n-heptane or n-octane/n-nonane mixtures and showed an R² of 1, see Figure 40 and Figure 41 in appendix B1. The RRF is 0.6581 for the n-heptane mixture and 0.6676 for the n-octane mixture, with the relation given in Equation 14. After dilution (approximately 1:9) the mixture was analysed using GC and the thiophene and n-nonane peaks were compared. The weight fraction of thiophene can then be calculated and the rest was assumed to be n-heptane/n-octane. Raw data from which the RRFs were obtained are shown in appendix B1.

$$\frac{A_{thiophene}}{A_{nonane}} = RRF * \frac{c_{thiophene}}{c_{nonane}}$$

Equation 14 relation of areas of thiophene to the internal standard and the concentration, using RRF

H-NMR

Before H-NMR measurements, the relaxation time (T1) of all the components had to be determined. This was done by dissolving using a 400 MHz NMR on an automated T1 protocol. One peak per component was integrated and the results were fitted according to Equation 15. [EMIM][MeSO₃] has a relaxation time of 5.234 s, [EMIM][MeSO₃] has a relaxation time of 6.222 s, thiophene has a relaxation time of 9.737 s, and octane has a relaxation time of 2.901 s. Therefore, the time between experiments needs to be at least 48.685 s.

$$M_z(t) = M_{z0} \left(1 - 2e^{-\frac{t}{T_1}} \right)$$

Equation 15 magnetization of the compounds in the system

The bottom layer was analysed using H-NMR because of the negligible vapour pressure of the ionic liquid, making GC impossible. The solvent used was deuterated methanol and due to the high relaxation time of thiophene, a high delay between scans was required, namely 50 seconds. This was to ensure that the peaks of the different scans were accurate reflections of their mole fractions.

Due to the limited availability of the machines and the long scanning times required, the experiments were measured at both 300 MHz and 600 MHz at different numbers of scans, for different systems, as shown below. All six experiments for a system were always done at the same number of scans and frequency.

- [EMIM][MeSO3]/n-heptane 20 scans 600 Mhz
- [EMIM][MeSO3]/n-octane 32 scans 600 MHz
- [EIM][NO3]/n-heptane 20 scans 600 MHz
- [EIM][NO3]/n-octane 32 scans 300 Mhz

Results

Mole fractions

The top layer was analysed using GC and checked for ionic liquid using H-NMR, because of the negligible vapour pressure of the ionic liquid showing no peak for the GC. No system had any ionic liquid present in the top layer.

Using the RRF of the n-heptane/n-nonane and n-octane/nonane for the n-heptane and n-octane systems respectively, the obtained (absolute) areas of the GC could be correlated to the weight fraction of thiophene, using Equation 14. The thiophene, n-heptane/n-octane and n-nonane peaks appeared left to right on the GC, of which the n-heptane/n-octane peak was clearly recognisable due to its height since it was the solvent of the system. For the n-heptane systems, a small impurity was present underneath the thiophene peaks. This area was measured from a blanc stock solution (no thiophene) and subtracted from the thiophene+impurity area. The impurity area has been measured a couple of times throughout the months. The mole fraction for the top layer was calculated from the masses that were measured when filling the GC vials and the obtained weight fractions. The GC results are shown in appendix B2.

The results of the bottom layer were obtained using H-NMR. Three peaks are integrated, which are the following for each of the different components, see Figure 8:

- 1. n-heptane or n-octane: six protons around 0.87-0.91 PPM for the two outer carbons of the molecule.
- 2. Thiophene: two protons on the second and third carbon around 7.1 PPM.
- 3. [EMIM][MeSO₃]: the three protons of the methyl of the anion, around 2.7 PPM.
- 4. [EIM][NO₃]: The two protons of the first carbon of the ethyl group connected to the nitrogen, around 4.3 ppm.



Figure 8 Protons of each component chosen for quantitative H-NMR analysis

The peaks were normalized on the ionic liquid peak and divided by their respective number of hydrogens. The corrected area of a peak, divided by sums of these corrected areas is the mole fraction of the specific molecule. The H-NMR results are shown in appendix B3.

Finally, the results of the top and bottom layers were combined to create the following graphs: a ternary plot for each of the four systems, which are presented at the section regarding NRTL, together with their regressed NRTL values. Furthermore, the selectivity and distribution were calculated using Equation 6 and Equation 7. In the figures that are discussed next, x_2^{HC} depicts the amount of thiophene in the hydrocarbon phase. The selectivity is shown in Figure 9 and Figure 11, for the n-Heptane and n-octane systems respectively. The obtained selectivity and distribution have been added to graphs also containing other work for comparative reasons. The sources for Figure 9 through Figure 12 are shown in appendix B4. All LLE results and selectivities and distribution coefficients are shown in appendix B5.

The shape of the selectivity and distribution show that the extractive performance of the ionic liquids increases with decreasing thiophene concentration (Mafi, Dehghani, & Mokhtarani, 2018). Although the nice downward shape, as one might expect from other experimental data, was not obtained. This is not a major issue because a closer look at Figure 9 and especially Figure 11 reveals that the lines of other works also tend to be bumpy but to a lesser extent. Moreover, the most important results are obtained from the tie-lines, which will be discussed later. Also for the distribution, which is shown in Figure 10 and Figure 12 for the n-Heptane and n-octane systems respectively, the obtained results do not show the steep curve as expected from other experimental work, this is again not an issue for the same reason as the selectivity. Moreover, fewer data points are used in this work. The next two sections further defend the obtained results, using a mass balance and the Hand and Othmer-Tobias correlations. Note that the experiments have been repeated until satisfactory results were obtained, to minimize the influence of human error.

Firstly, in Figure 9, the selectivity of both the ionic liquids in the n-heptane system, show very good selectivities. As can be seen, [EMIM][MeSO₃] has the better selectivity of the two ionic liquids and is only outperformed by [DMIM][MP], as was expected from the Matlab screening. The selectivity of [EIM][NO₃] is comparable to [BMIM][SCN] and [BMIM][BF₄]. It is expected that if more data points were created for the graph, the shape of the curve would have mimicked the others. This is because the performance of the solvent should go down when more solute is present.



Figure 9 Selectivity in thiophene/n-heptane system, with the selectivity

The distribution of the two ionic liquids in the n-heptane system is quite bad, as can be seen from Figure 10, where it can be seen that the explored ionic liquids only outperform one other ionic liquid, namely [DMIM][MP]. However, [EMIM][MeSO₃] still outperforms [EIM][NO₃]. The Matlab screening stated that [DMIM][MP] should be worse than [EMIM][MeSO₃] and [BMIM][SCN] better, which is indeed the case. Moreover, the shape of the curve is rather flat, i.e. not showing a clear improvement in extractive performance at lower thiophene concentrations. It could be the case that when more points are analysed, a more downward shape is obtained, as expected from the other data from the literature. However, as the concentration of thiophene increases, the distribution will remain more constant.



Figure 10 distribution coefficient in thiophene/n-heptane system

In Figure 11 the selectivity of the n-octane systems is shown. Again the great performance of $[EMIM][MeSO_3]$ can be seen in this graph. In this graph, in particular, the curves of other works also show the bumpy lines, see [BMPIP][DCA]. $[EIM][NO_3]$ is again the lesser ionic liquid of the two, however, its performance is still quite good. The other ionic liquid that was obtained by the Matlab screening is [BMIM][SCN] and is indeed outperformed by $[EMIM][MeSO_3]$. [BMIM][SCN] does significantly outperform $[EIM][NO_3]$, though. The second to last point (around $x_2^{HC}=0.4$) of the $[EMIM][MeSO_3]$ curve shows a large dip, compared to the next point. Either of these points is probably too high/too low, however as will be discussed in the subsequent sections the results overall are probably correct. More data points might give exclusion as to what point might be incorrect.



Figure 11 selectivity in thiophene/n-octane

Lastly, in Figure 12 the distribution of the n-octane system is shown. Again [EMIM][MeSO₃] outperforms [EIM][NO₃]. However, compared to the other ionic liquids their performance is mediocre. The only worse ionic liquids are [OHOHMIM][NTf₂] and [BMPIP][DCA]. In this graph, the downward shape is more accented than in the n-heptane distribution graph, so it can be seen that the distribution is improved with decreasing thiophene concentration. As expected from the Matlab screening, [BMIM][SCN] indeed outperforms [EMIM][MeSO₃]. It is expected that the line will flatten out more if they are extended with more data points on the right-hand side. It is unknown how far up the distribution can go at even lower thiophene concentration. However as is shown in the other literary data, it will probably reach a maximum and go down again as the concentration further decreases. It seems to be the case that the distribution knows a maximum that is not at infinite dilution.



Figure 12 distribution coefficient in thiophene/n-octane system

In summary, because of the high selectivities, compared to the ionic liquids of other studies, the ionic liquids studied in this work could prove to be quite promising, especially for [EMIM][MeSO₃]. The distribution is rather mediocre. For both the selectivity and distribution, [EMIM][MeSO₃] outperforms [EIM][NO₃]. Moreover, in the comparison between the tested ionic liquids and [BMIM][SCN] and [DMIM][MP], two ionic liquids that also popped up in the screening, the following results can be seen: The selectivity of the n-Heptane systems is better for [DMIM][MP] and worse for [BMIM][SCN], than [EMIM][MeSO₃] and [EIM][NO₃]. For the n-octane system, it can be seen that [BMIM][SCN] has better selectivity than [EIM][NO₃], but a worse selectivity than [EMIM][MeSO₃]. For the n-heptane system distribution, [BMIM][SCN] is superior to the tested ionic liquids and [DMIM][MP] is worse. In the n-octane case, [EMIM][MeSO₃] outperforms [BMIM][SCN], which in turn outperforms [EIM][NO₃]. Lastly, it can be seen that in this work fewer data points are obtained per system.

Mass balance

Because it is known that no ionic liquid was present in the top layer, all ionic liquid has to be in the bottom layer of the system. Because this amount is known, since it was measured when preparing the experiments, it is possible to calculate all other components in both the top and bottom layer. First, the amount of n-heptane or n-octane and the amount of thiophene in the bottom layer was calculated, using the obtained mole fractions. Subsequently, the amount of n-heptane or n-octane in the top layer

was calculated from the original added amount and the amount in the bottom layer. Lastly, the amount of thiophene in the bottom layer can be calculated from the amount of n-heptane or n-octane in the top layer, and their respective weight fractions. Lastly, the total amount of thiophene is related to the amount of thiophene which was originally added to the flask. These values all proved to be well below 10% and are depicted in appendix B5. This shows that the obtained mole fractions are valid.

Hand's and Othmer-Tobias correlation

The obtained results were analysed using both the Hand's and Othmer-Tobias correlation, see Equation 16 and Equation 17. In the equations, x and w refer to the mole and mass fractions respectively and a and b are the fitting parameters. A linear fit should be obtained, which is the case for all of the systems in this work, see Figure 13 and Figure 14. All R² are 0.99, for both correlations and all systems, further validifying the results.

$$\ln\left(\frac{x_2^{HC}}{x_3^{HC}}\right) = a + b \ln\left(\frac{x_2^{IL}}{x_1^{IL}}\right)$$

Equation 16 Hand's correlation (M. Z. M. Salleh, Hadj-Kali, Hashim, & Mulyono, 2018)

$$\ln\left(\frac{1 - w_3^{HC}}{w_3^{HC}}\right) = a + b \ln\left(\frac{1 - w_1^{IL}}{w_1^{IL}}\right)$$

Equation 17 Othmer-Tobias correlation (Gómez, Domínguez, Calvar, Palomar, & Domínguez, 2014; Othmer & Tobias, 1942)







Figure 14 Othmer-Tobias correlation lines

NRTL regression

Method and results

The entire NRTL regression was performed by Daili Peng. Non-random two liquid (NRTL) is a model to calculate activity coefficients of components in solution, with the excess Gibbs energy. It does so by using Equation 18 and Equation 19. τ_{ij} is a binary interaction parameter, which is determined by the minimization of an objective function, which is also the value which needs to be implemented into Aspen Plus, in the subsequent process design. An initial input of this parameter is required for the first calculation of the correct parameter. The initial input is largely decided based on experience. During NRTL regression the algorithm simultaneously finds the roots of the NRTL parameters, see Equation 19, and the roots of the material balance, equilibrium balance and the equation of summation, see Equation 22 to Equation 24, which it does by minimizing the objective function, Equation 20. In the end, the binary interaction parameters are obtained, as well as the new tie-lines. There are six different binary interaction parameters, three for each phase. α_{ij} is the non-randomness parameter, which is set between 0.2 and 0.47 (Z. Salleh et al., 2017), until the best result is obtained, which was at 0.3 for all systems. In Matlab minimization can be performed using the fmincon function. When an answer is obtained the root mean square deviation (RMSD) is calculated, if this is not acceptable (~1%) then it is further minimized. The adjusted R² for the correlation was >0.99 for all four systems.

At the end of the process, six different interaction parameters are obtained, for each of the four systems. It is important to note that the interaction parameters between thiophene and octane or heptane must be the same for both ionic liquids. All values are given in Table 2. The obtained ternary plots are shown in Figure 15, alongside their respective experimental tie line. Note that 1,2 and 3 refer to the ionic liquid, thiophene and n-heptane/n-octane, respectively. The NRTL results are shown in appendix C.

$$\frac{G^E}{RT} = \sum_i x_i ln \gamma_i$$

Equation 18 Relation between excess Gibbs energy and activity for a multi-component system (J. . Smith et al., 2005a)

$$ln\gamma_{i} = \frac{\sum_{j=i}^{n} \tau_{ji}G_{ji}x_{j}}{\sum_{k=1}^{n} G_{ki}x_{k}} + \sum_{j=1}^{n} \frac{x_{j}G_{ij}}{\sum_{k=1}^{n} G_{kj}x_{k}} \left(\tau_{ij} - \frac{\sum_{l=1}^{n} x_{l}\tau_{lj}G_{lj}}{\sum_{k=1}^{n} G_{kj}x_{k}}\right)$$

Where $\tau_{ij} = \frac{g_{ij} - g_{jj}}{RT} = \frac{\Delta g_{ij}}{RT}$, $G_{ij} = \exp(-\alpha_{ij}\tau_{ij})$, $\alpha_{ji} = \alpha_{ij}$

Equation 19 activity coefficient for an NRTL solution, with n components (Ilbeigi et al., 2014)

$$0Fa = \sum_{i}^{n=6} \sum_{j}^{m=3} \sum_{k}^{p=2} \left(x_{i,j,k}^{exp} - x_{i,j,k}^{cal} \right)^2$$

Equation 20 objective function a

$$OFx = RMSD = \sqrt{\frac{1}{N} \sum_{1}^{N} (x^{exp} - x^{cal})^2}$$

Equation 21 objective function x, also known as root-mean-square-deviation

$$x_i - (1 - \omega) x_i^{HC} - \omega x_i^{IL} = 0$$

Equation 22 Material balance (total fraction i – i in HC layer – i in IL layer = 0) (Z. Salleh et al., 2017)

$$x_i^{HC}\gamma_i^{HC}-x_i^{IL}\gamma_i^{IL}=0$$

Equation 23 Equilibrium equation (Z. Salleh et al., 2017)

$$\sum x_i^{HC} - \sum x_i^{IL} = 0$$

Equation 24 Equation of summation (Z. Salleh et al., 2017)

Table 2 NRTL parameters, N.B. 1=IL, 2=thiophene, 3=hydrocarbon, at T=298.15K

System	Δg_{12}	Δg_{13}	Δg_{23}	Δg_{21}	Δg_{31}	Δg_{32}	RMSD
	RT	RT	RT	RT	RT	RT	
[EIM][NO₃/C7	0.260	6.869	1.500	6.414	6.383	-0.131	0.0104
[EIM][NO₃/C8	0.521	5.293	1.756	6.987	3.840	-0.073	0.0092
[EMIM][MeSO ₃]/C7	-0.249	6.165	1.500	6.412	5.534	-0.131	0.0137
[EMIM][MeSO ₃]/C8	0.094	6.360	1.756	6.802	5.076	-0.073	0.0108



Figure 15 The experimental and NRTL regressed tie-lines for the four different systems.

Check-up

Using the work of (Marcilla, Reyes-Labarta, & Olaya, 2017) it can be checked if the results of the calculated LLE data is correct. The work of (Marcilla et al., 2017) focusses on the limitations of the common K-method on solving LLE NRTL equations. The K-method being a process that simultaneously solves the material balances and the isoactivity equilibrium condition (The sum of the difference between the activities of the two layers must be zero) (Marcilla et al., 2017). The limitations as defined by (Marcilla et al., 2017) are as follows:

- 1. Isoactivity is a necessary but not a sufficient condition for LLE. By which is meant that there are metastable solutions, which do satisfy the isoactivity condition, but are not stable. The solution is stable at the minimum Gibbs energy of mixing. (Marcilla et al., 2017)
- 2. Uncertainty in the isoactivity calculation. Two clear roots should be present in the Gibbs energy of mixing graph. If the Gibbs energy of mixing is wrong, incorrect tie-lines which satisfy the isoactivity condition could appear. (Marcilla et al., 2017)
- 3. Solutions are highly dependent on initial guesses. The algorithm requires an initial guess for the minimization of the objective functions. One problem is that multiple roots can be obtained during the process. Another problem is that due to the lack of experimental data regarding the activity of the systems, the validation is difficult. (Marcilla et al., 2017)
- 4. No guarantee of parameter consistency in all the composition space. The obtained NRTL parameters should not only accurately reproduce the experimental tie-lines, but also the number of miscibility regions. (Marcilla et al., 2017)

Since all the obtained graphs are similar in shape for all the four systems, only the [EIM][NO₃] with n-heptane system is shown here. The other graphs are presented in appendix D and the results discussed here also apply to those graphs. The graphs are generated from the obtained NRTL results, using a Matlab code supplied by (Marcilla et al., 2017).

The first three graphs are related to the Gibbs energy of mixing (G^M/RT). For this, the following must be true: For the miscible region, no common tangent of the Gibbs energy of mixing curve should be present (Marcilla et al., 2017), which is indeed the case when looking at Figure 16, since only one root is present. For the Gibbs energy of mixing curves containing the ionic liquid, a common tangent line is present, which does not lie on top of the curve (Marcilla et al., 2017). In Figure 17 a line can be drawn through the maximum at x(1)=0.1 and x(1)=1, and in Figure 18 a line can be drawn through the maximum at x(1)=0.2 and x(1)=0.8, meaning that the Gibbs energy of mixing curves are correct.



Figure 16 Gibbs energy of mixing curve for thiophene (2) and n-heptane (3) (left) Figure 17 Gibbs energy of mixing curve for [EIM][NO₃] (1) and thiophene (2) (right)



Figure 18 Gibbs energy of mixing curve for [EIM][NO₃] (1) and n-heptane (3)

The Miscibility boundary graphs, see Figure 19, is the easiest graph supplied by (Marcilla et al., 2017) and is also the most important graph. In this graph, one point (23, i.e. thiophene and n-heptane) should be in the homogeneous LLE region, and the other two should be in the heterogeneous region (Marcilla et al., 2017), where the homogeneous and heterogeneous refer to the liquid type (with or without ionic liquid). This is the case for all systems. The Tij and Tji depicted in the graphs are the same τ_{ij} and τ_{ji} depicted in Equation 19. Since all the graphs are up to the standards proposed by (Marcilla et al., 2017) for all four systems, it can be stated that the regressed NRTL parameters are correct.



Figure 19 NRTL miscibility boundary graph [EIM][NO₃] and n-heptane (left)

Figure 20 Gibbs energy of mixing curve for [EIM][NO₃] (1) and n-octane (3) (right)

Only one graph deviated from the other graph, namely the $[EIM][NO_3]$ -octane graph, see Figure 20. Although the same shape as Figure 18 and the 1-3 graphs from the $[EMIM][meSO_3]$ systems is not obtained, it can still be assumed that the shape is correct. In this particular case, the common tangent is between x(1)=0.01 and 1, i.e. only one LLE in this system. Moreover, as was stated the miscibility graph is the most important of the four graphs and this graph is correct for all four systems.

Process design

Stream quantification

A barrel of crude oil produces the following fractions: 42% gasoline, 22% diesel, 9% jet fuel, 5% fuel oil, 4% LPG and 18% other products (Cuttica, 2018). Because the experimental data for this work is obtained using n-heptane and n-octane, the focus is on light distillates (C5-C10). A barrel of crude oil contains 42 US gallons (159 litres). Shell Pernis processes about 404,000 barrels of crude oil every day, or about 750 L/s (Shell Nederland, n.d.). This means that the process size should be 0.42*0.750*3600=1134 m³/h of gasoline. Unfortunately, these streams are too big for proper process design and therefore it was decided to use 10 T/h of fuel, using the mass fractions as shown in Table 3. This is similar to the works of (Song et al., 2018), which obtains good comparison abilities.

On average the sulphur content in crude oil is 1.1wt%. In the different fractions, this amount increases with the boiling point of the said fraction (Cuttica, 2018). For this project 360 mg/L thiophene is assumed, which is the amount of sulphur in the 90 to 140°C fraction from Arab oil. Of this 360 mg/L 3.9, 72, 222.1 and 61.9 mg/L are related to methyl-, ethyl-, propyl and butyl thiophene, respectively. No normal thiophene is present in this fraction range (D. Singh, Chopra, Mahendra, Kagdiyal, & Saxena, 2016). 50% to 95% of sulphurs in crude oil consists of thiophenes (Kilbane & Le Borgne, 2004). Other sulphur compounds in oil are mercaptans, sulphides, disulphides and sulfoxides (Cuttica, 2018). The 260 mg/L of thiophene corresponds to 520 ppm.

Fuel compound	Mass flow (kg/h) (Shell)	Mass fraction
n-heptane	3940248.8	0.5
n-octane	3940248.8	0.5
Thiophene	408.24	520 PPM
Total	784506	1

Table 3 Fuel flow which needs desulfurization as based on the (Shell Nederland, n.d.; D. Singh et al., 2016)

Ionic liquid process

Properties Aspen

Because the model is working on the NRTL-2 model (NRTL with two data sets one for n-heptane and one for n-octane) some settings must be changed for Aspen to understand the difference between the liquid and ideal gas heat capacity. To do this you need to take the following steps: select properties, select methods, select NRTL-2, select subordinate property under property type, change DHL to DHL09 and lastly save the method under a new name. More information regarding this is in the Aspen Plus Help centre.

The constants given in Table 34 and Table 35 for Equation 53 to Equation 57 was implemented into the temperature-dependent property data of Aspen Plus, see appendix E. The following models were used: For liquid heat capacity CPLPO, for ideal gas heat capacity CPIGPO, for the heat of vaporization DHVLPO, for the viscosity MULAND, for the surface tension SIGDIP, for the density (molar volume) VLPO, and for the thermal conductivity KLDIP. The vapour pressure of the system was estimated by Aspen and generates the PLXANT model. The vapour pressure plot shows an exponential curve through a negligible pressure at room temperature and a pressure of 1 bar at the boiling point, as expected for an Antoine equation. The pure properties were also entered, namely: the boiling point, the molecular weight, the critical temperature and pressure, the acentric factor, the critical compressibility factor, and the critical volume, see appendix E. The latter three were obtained from the work of (Valderrama & Rojas, 2009).

The entered temperature values were compared to the experimental and calculated property data and it showed the following. For [EMIM][MeSO₃] the density had a deviation of 0.02% between the fit given in Table 34 and the values calculated in Aspen Plus. For the liquid heat capacity $2.53*10^{-4}$ %, for the ideal gas heat capacity 0.10%, for the viscosity 0.03%, for the surface tension 0.03% and for the thermal conductivity 4.5%. Because of these low deviations, the property data was entered properly into the program. For [EIM][NO₃] the values are 0.06%, 0.014%, 1.13%, 0.00%, 0.01% and 6% respectively, with the fit data shown in Table 35. Again, the deviations are sufficiently low to assume that the property data is correct.

NRTL Aspen

Before the process design was started the NRTL values entered into Aspen Plus are checked. As can be seen from the triangle plots in appendix F, the tie-lines generated in Aspen (in blue) overlap with the experimental tie-lines, except for some small deviations on the right-hand side of the triangle plots. This deviation is because some ionic liquid is present in the hydrocarbon layer of the system according to the NRTL values (0.2-0.4%), which is not the case for the experimental values. This issue was fixed using a separator block in the Aspen Plus process model.

The sensitivity and distribution plots were also recreated in Aspen plus, using an extraction column using the NRTL model with 10 stages. The model does not contain the beforementioned separator yet. The flows were the same masses as from the experimental section, but now it is all in kg/h instead of grams. As can be seen, the sensitivity has a far steeper curve downwards, see Figure 21, compared to the experimental results, see Figure 9 and Figure 11. The order of magnitude of the sensitivity is the same. The distribution as obtained by Aspen Plus shows a very similar curve as the experimental work, see Figure 22, Figure 10 and Figure 12 respectively. Overall, it is deemed that the NRTL values implemented into Aspen Plus show satisfactory overlap with the experimental work and can be used for further process design.



Figure 21 Aspen calculated sensitivity (left)



Extractor

Aspen

The extractor model in Aspen is only appropriate for rating calculations, i.e. only calculations of the different phases and no scaling at all (Aspen Plus, n.d.-a). First, the number of trays had to be determined, which is done in a similar fashion as (Song et al., 2018). The extract unit operation was put on a certain number of stages and the required amount of solvent (IL) was determined through the Aspen Plus trial and error method 'design spec'. The goal is to reach a thiophene concentration

below 10 ppm as determined by EU standards for sulphur-free fuels (Dieselnet, n.d.). Furthermore, in the experiments it was found that no ionic liquid was present in the hydrocarbon layer after settling, unfortunately it was not possible to reproduce this when reducing the NRTL values from the experimental work. Therefore, it was decided to implement a separator after the extraction unit operation. In this separator, all the ionic liquid was removed and rerouted to the bottom ionic liquid stream, see Figure 24. After determining the amount of ionic liquid required for each number of stages, a graph was made which shows the solvent to feed ratio, versus the number of stages, see Figure 23. Lower solvent to feed ratio is better. It was decided to use 10 theoretical stages for both [EMIM][MeSO₃] and [EIM][NO₃] for a fuel flow of 10 T/h. this results in a [EMIM][MeSO₃] feed of 26027 kg/h, see appendix G1.



Figure 23 Solvent to feed ratio for different number of stages of the extraction column



Figure 24 A 'fake' separator reroutes all unintentional ionic liquid to the bottom stream

Using the NRTL model the profiles/composition of the 1st liquid (the ionic liquid) and the 2nd liquid (nheptane and n-octane) for each tray was determined by Aspen Plus. Furthermore, the software also determined the flow of the 1st and 2nd liquid on each tray, as well as their respective enthalpies. The 1st liquid flows downwards, and the 2nd liquid flows upwards. Using this data, the dimensions of a column can be determined.

Extractor types

First, an extractor type has to be chosen. The options are between static extraction columns, mixersettlers, rotary-agitated columns, reciprocating-plate columns, pulsed columns and lastly centrifugal columns (Frank et al., 2008). Because of the moderate (several 100 cP) viscosity of the ionic-liquid and the low viscosity of the hydrocarbon layer the rotary-agitated columns are best suited for this system (Frank et al., 2008). Other features of this column type are the moderate capital cost and low operating cost compared to other columns (Frank et al., 2008). Furthermore, it has a high number of possible theoretical stages (Frank et al., 2008). There are different Rotary-agitated columns available, namely the rotating disc contactor (RDC), asymmetric rotating disc contactor (ARDC), Oldshue-Rushton column, Scheibel column and the Kühni column (Frank et al., 2008).

The Scheibel column consists of wire mesh packed sections, with shrouded impellers in the middle. Each section is surrounded by baffles, see Figure 25A. Later versions of the column had the wire mesh replaced with agitated sections because the mesh was prone to fouling (Frank et al., 2008). The Scheibel column is particularly useful for extraction requiring a high number of theoretical stages/height (Frank et al., 2008). Furthermore, its high efficiency also makes it suitable for towers that are indoors and cannot be as high as towers outdoors (Frank et al., 2008). The Scheibel column has a maximum capacity of about $25 \text{ m}^3/\text{h/m}^2$ and has a typical maximum diameter of 3 m (Frank et al., 2008). Lastly, the column type is not recommended for systems that tend to emulsify (Kochmodular, n.d.).

The rotating disc contactor (RDC), shown in Figure 25B, is together with its asymmetric variant (ARDC) the only column that uses a spinning disc instead of an impeller, of all columns that are discussed here. The disc of the RDC uses the shear forces on the disc to disperse the liquids (De Haan & Bosch, 2013). The RDC is already used for sulfolane extraction processes, which the ionic liquid aims to replace (De Haan & Bosch, 2013). The RDC has horizontal, doughnut shape, stators surrounding the edge of the tray, because of this open design it has back mixing problems reducing mass transfer performance (Frank et al., 2008). The RDC has a maximum specific throughput of 35 m³/h/m² and a typical maximum diameter of 4 m (Frank et al., 2008). Lastly, the column type is not recommended for systems that tend to emulsify (Frank et al., 2008). The ARDC, shown in Figure 25C, is used in the pharmaceutical industry and employs a compartment for mixing and settling (Crowell, 1997).

The Oldshue-Rushton column, shown in Figure 25D, is again very similar to the Scheibel column, however, each section is much larger, because of this each stage can be seen as a separate mixer-settler unit (Crowell, 1997). The Oldshue-Rushton column is also very similar to the RDC because of its open design, however, it does also have a vertical baffle, which has the RDC does not have (Robbins & Cusack, 1997). The baffles form a circle around the entire edge of each stage (De Haan & Bosch, 2013; Visscher, 2013). The Oldshue-Rushton column is capable of handling solids in suspension (Asadollahzadeh, Shahhosseini, Torab-Mostaedi, & Ghaemi, 2016). Because of the large sections, the tower has a higher height to diameter ratio than other towers (Robbins & Cusack, 1997). Because in this thesis' process the ionic liquid enters the top of the tower, the greater height means a major drawback in terms of pumping power required.

The Kühni column, depicted in Figure 25E, again uses shrouded impellers (Frank et al., 2008). The sections are closed off with perforated plates (Frank et al., 2008). Its design of shrouded impellers reduces the back mixing between sections. The Kühni column has a typical diameter of a maximum of 3 meters and a maximum specific capacity of 40 m³/h/m² (Frank et al., 2008). Its design is quite similar to the Scheibel column, but the design is simpler (Crowell, 1997).

Of all the columns mentioned the RDC has the highest maximal hourly throughput, with 450 m³/h (Frank et al., 2008). Furthermore, it has a relatively simple design, compared to the other column. Moreover, because it is already used in sulfolane processes there is already a familiarity with this column. For these reasons, the RDC is chosen as the column that is used in this thesis.



Figure 25 Different agitated extraction columns: Scheibel column A, rotating disc column B, asymmetric rotating disc column C, Oldshue Rushton column D, Kühni column E (De Haan & Bosch, 2013)

Column design

As mentioned the rotating disc column is used for this process, in Figure 26 and Figure 27 more detailed looks at the RDC are shown. For the design a variety of things are important: The Sauter mean drop diameter, d_{32} , which is the diameter as related to the volume (3) and area (2) of a particle (S. A. F. Onink, 2011); The dispersed phase hold up (volume fraction), ϕ_d (S. A. F. Onink, 2011); the interfacial tension; the system dispersion coefficients and the pressure drop.



Figure 26 A more detailed look at the RDC (Frank et al., 2008) (left)

Figure 27 Another detailed look at an RDC (S. A. F. Onink, 2011) (right)

The dispersed phase

First, it needs to be determined which phase is dispersed and which is continuous, for which Equation 25 can be used. For χ <0.3 the light phase is dispersed; for χ =0.3-0.5 the light phase is probably dispersed; for χ =0.5-2.0 either phase can be dispersed, with the possibility of phase inversion; for χ =2.0-3.3 the heavy phase is probably dispersed and lastly, for χ >3.3 the heavy phase is always dispersed (Frank et al., 2008). For this, the properties at 25°C and 1 bar were assumed. The volume sizes were calculated by running the two different phase sizes as defined in the Aspen section through a mixer unit operation in Aspen Plus, where the feed of the mixer is also the feed of the extraction column. This yielded the total volume and the volumes of the different phases. For the [EMIM][MeSO₃]-system it was determined that χ =3.25 and the dispersed phase is the ionic liquid phase. The calculation can be found in appendix G2.

$$\chi = \frac{\varphi_L}{\varphi_H} * \left(\frac{\rho_L \eta_H}{\rho_H \eta_L}\right)^{0.3} = \frac{\varphi_L}{1 - \varphi_L} \left(\frac{\rho_L \eta_H}{\rho_H \eta_L}\right)^{0.3}$$

Equation 25 determination of dispersed phase, with L being the light phase and H the heavy phase, φ the volume fraction (hold up), η the viscosity and ρ the density (Frank et al., 2008).

The Sauter mean diameter

The Sauter mean diameter is as mentioned the volume-to-surface average diameter of a spherical particle, see Equation 26 (Frank et al., 2008). It is difficult to determine the actual diameter of a particle when agitation is used in the tower (Frank et al., 2008). If the rotor Reynolds number is higher or equal to 10000 the drop size is a function of the rotational speed, the flow rates and the tower height, with the rotor Reynolds number depicted in Equation 29 (S. A. F. Onink, 2011). Below a rotor Reynolds number of 10000, the diameter is a function of the interfacial tension and buoyancy forces, controlling the size of the droplets through collisions, see Equation 27 (S. A. F. Onink, 2011). Lastly, the Sauter mean diameter is also directly correlated to the specific surface area of the mass transfer between the phases, as shown in Equation 28 (Frank et al., 2008).

$$d_{32} = \frac{\sum N_i d_i^3}{\sum N_i d_i^2}$$

Equation 26 Sauter mean diameter, with Ni the number of particles with diameter di (Frank et al., 2008).

$$d_{32} = C \left(\frac{\gamma_{i,T}}{\Delta \rho g}\right)^{0.5}$$

Equation 27 Sauter mean diameter for $Re_R \le 10000$, with $\gamma_{i,\tau}$ the interfacial tension and C a constant dependent on mass transfer, column geometry and the liquid-liquid system (S. A. F. Onink, 2011)

$$d_{32} = \frac{6\varepsilon\varphi_d}{a}$$

Equation 28 Sauter mean diameter, with ε the void fraction (volume excluding trays etc.), a the specific surface area per volume and φ_d the holdup of the dispersion (Frank et al., 2008)
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$$Re_R = \frac{ND_R^2\rho_c}{\eta_c}$$

Equation 29 rotor Reynolds number, with N the rotational speed in s^{-1} , D_R the diameter of the rotor, and the subscript c denoting the continuous phase, which is the hydrocarbon phase for the [EMIM][MeSO₃]-system (S. A. F. Onink, 2011)

The work of Kumar et al. gives a unified formula for the determination of the drop size for a variety of extraction columns, namely (A)RDC, Kühni, Wirz-II and pulsed/Karr columns (A. Kumar & Hartland, 1996). In Equation 30 this correlation is shown, where H_c is the height of a tray, e the fractional free cross-sectional area, as shown in Equation 31. The first constant, C1, is related to the mass transfer and is equal to 1 if mass transfer occurs from the continuous to the dispersed case, which is the case for the system of this project. C2 and C3 are related to the physical properties of the droplets (S. A. F. Onink, 2011) The dimensions of the column H_C, D_s, D_R and D_C are shown in Figure 28. For Equation 30 the power dissipation per unit mass, ϵ , is also required, which is in turn related to the power number N_P, as shown by Equation 32 and Equation 33 respectively (A. Kumar & Hartland, 1996; S. A. F. Onink, 2011). The different constants for the different equations are shown in Table 4, which only applies to RDC, other columns have different constants and are depicted in the work of (A. Kumar & Hartland, 1996). For Equation 30 the reported average absolute relative error is 22.4% for the RDC (A. Kumar & Hartland, 1996). Because no experimental work related to drop size was done, the parameters as determined by (S. A. F. Onink, 2011) have to be used, because of his work with a different ionic liquid, see Table 4. The final obtained droplet diameter should be in the range of 0.5 to 1.5 mm (S. A. F. Onink, 2011).

$$\frac{d_{32}}{H_C} = \frac{C_1 e^{n_1}}{\left(C_2 \sqrt{\frac{\gamma_{i,T}}{\Delta \rho g H_C^2}}\right)^{-1} + \left(C_3 \left[\left(\frac{\epsilon}{g}\right) \left(\frac{\rho_C}{g \gamma_{i,T}}\right)^{0.25}\right]^{n_2} \left[H_C \left(\frac{\rho_C g}{\gamma_{i,T}}\right)^{0.5}\right]^{n_3}\right)^{-1}}$$

Equation 30 Unified correlation for the Sauter mean diameter (A. Kumar & Hartland, 1996)

$$e = \left(\frac{D_S}{D_C}\right)^2$$

Equation 31 fraction free cross-sectional area for RDC (S. A. F. Onink, 2011), see Figure 28

$$\epsilon = \frac{4P}{\pi D_c^2 H_c \rho_c}$$

Equation 32 the power dissipation per unit mass in a rotary-agitated column, with P the power input per agitator (A. Kumar & Hartland, 1996)

$$N_P = \frac{C1}{Re_R} + C2 \left(\frac{1000 + 1.2Re_R^{n2}}{1000 + 3.2Re_R^{n2}}\right)^{n1} = \frac{P}{N^3 D_R^5 \rho_c}$$

Equation 33 correlation between power number Np, power per agitator P and the rotary Reynolds Number Re_R (A. Kumar & Hartland, 1996; S. A. F. Onink, 2011)



Figure 28 different annotations of dimensions in the RDC (S. A. F. Onink, 2011)

Table 4 constants for equations, which only apply to RDC, with c the continuous phase and d the dispersed phase (A. Kumar & Hartland, 1996).

Constant	Equation 30 (A. Kumar & Hartland, 1996)	Equation 30 (S. A. F. Onink, 2011)	Equation 33
C1	1 (c to d) or 1.29 (d to	1 (c to d) or 1.29 (d	109.36
	c)	to c)	
C2	2.54	2.54	0.74
C3	0.97	2.21	-
n1	0.64	0.64	3.30
n2	-0.45	-0.45	0.72
n3	-1.12	-1.12	-

Hold-up

As already shown in Equation 28, the hold-up is related to the diameter of the particle, which varies with the dimensions of the stages and the rotational speed of the rotors, as shown by Equation 30 through Equation 33. It is possible to measure the hold-up experimentally, however, this was not done.

A variety of hold-up correlations have been created over the years, where (Morís, Díez, & Coca, 1997) determined that the work of (Murakami, Misonou, & Inoue, 1976) showed the 'best' fit, with an average error of 48% compared to their experimental results of their kerosene/water system. Unfortunately, their model does not include the Reynolds number, i.e. it does in no way take the viscosity into account (Murakami et al., 1976). The second-best formula does take viscosity into account and is an option. This is the work of (A. Kumar & Hartland, 1987), with no mass transfer, which showed a deviation of 65% from the kerosene/water system (Morís et al., 1997). Equation 34 gives the hold-up according to (A. Kumar & Hartland, 1987) for a system with no mass transfer. Because the mass transfer in this paper is very low (thiophene concentration goes from 520 to 10 ppm) this formula could be used.

$$\begin{split} \varphi_d &= \left(570.53 + 747.78 * \left(\frac{N^2 D_R}{g}\right)^{1.28}\right) \left(\frac{D_s^2 H_c^2 \rho_c g}{D_c^2 \gamma_{i,T}}\right)^{-0.45} \left(\frac{\Delta \rho}{\rho_c}\right)^{-0.58} \\ & * \left(\frac{\eta_c g^{0.25}}{\rho_c^{0.25} \gamma_{i,T}^{0.75}}\right)^{0.85} \left(\frac{U_d^4 \rho_c}{g \gamma_{i,T}}\right)^{0.22} \left(1 + \frac{U_c}{U_d}\right)^{0.35} \end{split}$$

Equation 34 dispersed phase hold-up calculation for a system with no mass transfer (A. Kumar & Hartland, 1987, 1989; Morís et al., 1997)

However, because the first term of Equation 34 the hold-up is very unrealistic for the proposed system, at normal rotational speeds, e.g. at a rotational speed of 8 rounds per second, the dispersed phase hold-up was only 2.7%. Therefore, another correlation is used, namely, the one proposed by (S. A. F. Onink, 2011), see Equation 35. The correlation of (S. A. F. Onink, 2011) has the added benefit of being designed from experimental work with an ionic liquid, making it more suitable to the application of this work. This is because the ionic liquid in his work also has high viscosity (203 cP for [4-mebupy][BF4]) (S. A. F. Onink, 2011). Furthermore, the density and interfacial tension in the work of (S. A. F. Onink, 2011) is also in the same order of magnitude as in this work. In this equation, Π allows for the input of power per unit mass, Φ the phase flow rates, Ψ the physical properties and Γ the geometric dimensions of the column. In particular Ψ is an important part of this formula, which accounts for the viscosity difference between the continuous and dispersed phase, which is very large in the case of ionic liquid systems. This equation shows more realistic values of hold-up, namely 24.1% instead of 2.7%. The coefficients are especially optimized for an ionic liquid in the work of (S. A. F. Onink, 2011). The ionic liquids used by his work are [3-mebupy][DCA] and [4-mebupy][BF4]. Lastly, the hold-up and the superficial velocity can be related as shown in Equation 36 (A. Kumar & Hartland, 1992).

$$\varphi_{d} = \Pi \Phi \Psi \Gamma = \left(0.19 + \left(\frac{\epsilon}{g} \left(\frac{\rho_{c}}{g\gamma_{i,T}} \right)^{0.25} \right)^{-0.20} \right) \\ * \left(\left(U_{d} \left(\frac{\rho_{c}}{g\gamma_{i,T}} \right)^{0.25} \right)^{1.09} \exp\left(7.13U_{c} \left(\frac{\rho_{c}}{g\gamma_{i,T}} \right)^{0.25} \right) \right) \\ * \left(\left(\frac{\Delta \rho}{\rho_{c}} \right)^{-0.85} \left(\frac{\eta_{d}}{\eta_{c}} \right)^{-0.18} \right) * \left(\left(\frac{D_{R}}{H_{c}} \right)^{0.62} e^{-0.26} \left(H_{c} \left(\frac{\rho_{c}}{g\gamma_{i,T}} \right)^{0.5} \right)^{0.25} \right) \right)$$

Equation 35 dispersed phase hold-up formula as proposed by (S. A. F. Onink, 2011)

$$u_c = \frac{U_c}{1 - \varphi_d}$$
 and $u_d = \frac{U_d}{\varphi_d}$

Equation 36 relation between true velocity u and superficial velocity with the dispersed phase hold-up (A. Kumar & Hartland, 1992)

Interfacial tension

As already shown in Equation 30 and Equation 34 the interfacial tension, $\gamma_{i,T}$, is an important factor for the determination of the droplet size. Normally the interfacial tension is determined using a tensiometer (S. A. F. Onink, 2011). One option would be to use the OWRK method, see Equation 37, which uses the surface tensions of the different chemicals in the system, as well as the polar and dispersive component of the different chemicals, as shown in Equation 38 (Dataphysics Instruments GmbH, n.d.). Because the polar component of both n-heptane and n-octane is equal to 0, the polar factor cancels out of Equation 37, however, it is still necessary to know how big the dispersive component is of the ionic liquid surface tension.

$$\gamma_{1,2,T} = \sigma_1 + \sigma_2 - 2\left(\sqrt{\sigma_1^d \sigma_2^d} + \sqrt{\sigma_1^p \sigma_2^p}\right)$$

Equation 37 Owens, Wendt, Rabel, Kaelble (OWRK) method of determining interfacial tension using surface tension (Dataphysics Instruments GmbH, n.d.)

$$\sigma = \sigma^d + \sigma^p$$

Equation 38 Surface tension of a compound with its dispersive component and polar component

(Zhang, Wang, & Hu, 2010) determined the interfacial tensions of an ionic liquid-alkane system, where they used [C₅MIM][PF₆], [C₆MIM][PF₆], [C₈MIM][PF₆] as ionic liquids and n-hexane and n-heptane as alkane. They determined that increasing the side chain of the alkyl-methylimidazolium cation increases the dispersive component of the surface tension, as expected (Zhang et al., 2010). This effect was larger in the n-hexane systems than in the n-heptane systems (Zhang et al., 2010). For the n-heptane system, the factor of the dispersive component for the surface tension is as follows: 73.6% ($\sigma^d = 0.736 * \sigma$), 73.9% and 80.0% for [C₅MIM][PF₆] and [C₆MIM][PF₆], [C₈MIM][PF₆] respectively, at 283.15 K (Zhang et al., 2010). Because this thesis uses [EMIM][MeSO₃] and [EIM][NO₃] as ionic liquids, which an ethyl side chain and no side chain respectively, the dispersive component of both ionic liquids is assumed to be 73% and 72% respectively. The surface tensions for the ionic liquids are reported in appendix E2, the surface tension for the alkane is of n-heptane and obtained from Aspen Plus. For the [EMIM][MeSO₃]-system the interfacial tension is about 0.015 N/m and for the [EIM][NO₃]-system it is about 0.026 N/m, according to the OWRK method, see Figure 29.



Figure 29 interfacial tension from surface tension using the OWRK method, for [EMIM][MeSO₃]

Flooding

In extraction, the counter-current flow is important for mass transfer. When this counter-current flow gets blocked by the accumulation of dispersed phase droplets, flooding occurs (S. A. F. Onink, 2011). The formula for the hold-up at the flooding point is shown in Equation 39. Because this is an experimental correlation, no calculations regarding flooding can be done. The only estimation to check for flooding is by looking at the superficial velocities of the system, which should be in the same order of magnitude.

$$\varphi_f = \frac{\left(\left(\frac{U_d}{U_c}\right)^2 + 8 * \frac{U_d}{U_c}\right)^{0.5} - 3 * \frac{U_d}{U_c}}{4\left(1 - \frac{U_d}{U_c}\right)}$$

Equation 39 Hold-up at the flood point using the superficial velocities (U) of the dispersed and continuous phase (S. A. F. Onink, 2011)

Entrainment

Entrainment is the phenomenon of liquid being transported to the tray above by the gas flow (Kister et al., 2008). Because the system being designed is a liquid-liquid system this phenomenon is ignored, although some gas is present in the shape of hydrocarbon vapour.

Axial dispersion coefficient

The axial dispersion coefficient is a means of determining the amount of back mixing in the system and is used in very basic extractor design (A. Kumar & Hartland, 1992; Morís et al., 1997; S. A. F. Onink, 2011). For the purposes of this paper, it is checked if the obtained value is realistic because no experimental work is done. In Equation 40 the reciprocal of the continuous-phase Péclet number is calculated, which has a typical value between 1 and 4 (A. Kumar & Hartland, 1992; Morís et al., 1997). The Péclet number gives the ratio between mass transport via convection and mass transport via diffusion (Beek, Muttzall, & Van Heuven, 2000b). (Morís et al., 1997) determined that the most accurate equation is given by (A. Kumar & Hartland, 1992), see Equation 40 for the continuous phase, with an absolute average relative error of 4.8%. Meanwhile, the far easier model of (Westerterp & Landsman, 1962) shows an error of 5.8%, see Equation 41. In this work, the equation provided by (A. Kumar & Hartland, 1992) is used, see Equation 40.

$$\frac{1}{Pe_c} = \frac{E_c}{u_c H_c} = 0.42 + \frac{0.29 * U_c}{U_d} + \left(\frac{0.0126 * ND_R}{U_c} + \frac{13.38}{3.18 + \frac{ND_R}{U_c}}\right) \left(\frac{U_c D_R \rho_c}{\eta_c}\right)^{-0.08} \left(\frac{D_c}{D_R}\right)^{0.16} \left(\frac{D_c}{H_c}\right)^{0.10} \left(\frac{D_s}{D_c}\right)^2$$

Equation 40 axial dispersion coefficient for an RDC, for the continuous phase (A. Kumar & Hartland, 1992; Morís et al., 1997)

$$\frac{E}{u_c H_c} = 0.5 + 0.0065 * \frac{ND_R}{U_c}$$

Equation 41 axial dispersion coefficient for an RDC (Morís et al., 1997; Westerterp & Landsman, 1962)

There is also a relation for the dispersed phase axial dispersion coefficient, given in Equation 42. This relation uses the true velocities instead of the superficial velocities; however, these can be correlated with each other using the hold-up as shown in Equation 36. The value for the dispersed phase axial dispersion coefficient should be between 0 and 10 (A. Kumar & Hartland, 1992).

$$\frac{1}{Pe_d} = \frac{E_d}{u_d D_R} = \frac{0.30(u_c + u_d)}{u_d} + 9.37 \left(\frac{ND_R}{u_d}\right)^{-0.48} \varphi_d^{-0.90} \left(\frac{D_R^2 \Delta \rho g}{\gamma_{i,T}}\right)^{-0.64} \left(\frac{D_C}{D_R}\right)^{0.70}$$

$$for \ 6 < \frac{ND_R}{u_d} < 230$$

Equation 42 axial dispersion coefficient for an RDC, for the dispersed phase (A. Kumar & Hartland, 1992)

Pressure drop

No literature was found about calculating pressure drop for an RDC. The pressure drop of the system is divided into a few components: the pressure drop of the counter-current flow and the height of the tower, the pressure drop due to shear resistance with the wall and lastly the pressure drop due to the stators and rotor disc, for which the mechanical energy balance can be used as shown in Equation 43, which can be reduced to Equation 44 for constant velocity. In this system 2 denotes the top of a stage and 1 the bottom. The equation has a couple of unknowns, namely the energy dissipations and the frictional losses. It is assumed that no energy dissipation occurs in the system and that the energy dissipation, ϵ , which was seen earlier relates to the droplet size. The frictional losses are from the wall,

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the rotor and the stator and are factored into the equation using Equation 46, where Fanning's friction factor is determined from the Reynolds number as shown in Equation 47 for laminar flow and Equation 48 for turbulent flow. It is important to note that in Equation 46 the diameter is the hydraulic diameter, i.e. the diameter of the wetted surface (Van der Akker & Mudde, 2014). For the case of the RDC, this means that it included the wall of the column and the side of the rotor shaft. The rotor Reynolds number is used as determined in Equation 29. The friction loss factor K_w is determined for the stator and rotor using Equation 49 and Table 5 respectively. It should be noted that the vast majority of the pressure drop of the system is due to the hydrostatic pressure (99%) and the remainder of the pressure drop is due to friction.

$$0 = -\left(\frac{p_2 - p_1}{\rho} + g(h_2 - h_1) + \frac{1}{2}(\langle u_2 \rangle^2 - \langle u_1 \rangle^2)\right)\phi_m + \phi_A - E_{fr}\phi_m$$

Equation 43 Mechanical energy balance (Beek, Muttzall, & Van Heuven, 2000a; Van der Akker & Mudde, 2014)

$$\Delta p = -\rho g H_C - E_{fr}$$

Equation 44 pressure drop at a constant velocity

$$\tau = \frac{\varepsilon V_c}{\phi_V}$$

Equation 45 residence time in the column, where the void fraction is obtained by calculating the volume of stators, rotors and the rotating shaft

$$E_{fr} = \sum_{i} \left(4f \frac{1}{2} \langle u \rangle \frac{H_C}{D_{C,hyd}} \right)_i + \sum_{j} \left(K_w \frac{1}{2} \langle u \rangle \right)_j, \text{ with } D_{C,hyd} = D_C - D_{shaft}$$

Equation 46 energy loss due to friction (Beek et al., 2000a)

$$4f = \frac{64}{Re_R}$$
 for laminar flow

Equation 47 Fanning's friction factor for laminar flow (Beek et al., 2000a)

 $4f = 0.316 Re_R^{-0.25}$ for turbulent flow

Equation 48 Fanning's friction factor for turbulent flow (Beek et al., 2000a)

$$K_{w,stator} = 0.45 \left(1 - \frac{A_C - A_S}{A_C} \right) = 0.45 \left(2 - \frac{A_S}{A_C} \right)$$

Equation 49 friction loss factor for a stator ring (Beek et al., 2000a)

Table 5 friction loss factor for a rotor

A_R/A_C	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
Kw	226	47.8	17.5	7.8	3.75	1.80	0.80	0.30	0.06

In Aspen plus the pressure drop over the extractive section was implemented into the extraction block directly. The pressure drop over the top settler was implemented as a valve with a set pressure drop. The pressure increase over the bottom settler was implemented using a pump with a set pressure increase. As mentioned earlier a separator is present to move all the ionic liquid from the top stream to the bottom stream. This stream of ionic liquid is also connected to a pump to correct its pressure. See Figure 30.



Figure 30 The extraction column with the separator moving the ionic liquid from the top to the bottom stream and the pumps+valve to correct for the pressure drops.

Minimum rotational speed

(Leng & Calabreses, 2004) created an overview of formulas to determine the minimum rotational speed to obtain a liquid-liquid dispersion in a baffled vessel. The RDC can in a way be seen as a series of baffled vessels, where the rods holding the stator rings are the baffles. The best formula, in the opinion of (Leng & Calabreses, 2004), for determination of the minimum rotational speed is given by (Skelland & Seksaria, 1978), see Equation 50. The preference for this formula is due to the application to a variety of different stirred vessels with different impeller types (Leng & Calabreses, 2004). Unfortunately, no spinning disc impeller was available, so this formula is only used as an indication of the minimal speed. For the dimension that is used in the design section, this rotational speed is about 0.5 RPS for both ionic liquids. However, this is only to indicate how low the rotational speed could go, roughly, and it is difficult to say if this holds any merit for this thesis' system. Proper experimental work should be done to determine this speed accurately.

$$\frac{N_{min} D^{0.5}}{g^{0.5}} = 15.3 \left(\frac{H}{D}\right)^{0.39} \left(\frac{\eta_c}{\eta_d}\right)^{\frac{1}{9}} \left(\frac{\Delta \rho}{\rho_c}\right)^{0.25} \left(\frac{\gamma_{i,T}}{D^2 \rho_c g}\right)^{0.3}$$

Equation 50 minimum rotational speed of the stirred vessel, with a rotor impeller type at the interface of the two different phases (Skelland & Seksaria, 1978)

RDC Design

Using all the previously obtained equations and knowledge of the orders of magnitude, the column is designed through trial and error, with all parameters shown in Table 38, in appendix G3. This is because no literature was found on the theoretical design of an RDC. (S. A. F. Onink, 2011) reports a rotational speed 640 RPM for his ionic liquid system, however this speed resulted in a too high axial dispersion of the continuous phase (1/Pe_c), therefore a slightly lower speed was used: 8.5 RPS (510 RPM). Although a lower speed (3 RPS) generates plausible numbers for the other equations, it is unclear if the equations provided by (S. A. F. Onink, 2011) are meant to be used at lower rotational speeds, therefore, a higher speed was used to better mimic his designs. Next to the dimensions of each stage, the impeller Reynolds number was determined, which in turn calculated the power number and subsequently the power of the impeller. This power is important, since it plays a large part in the droplet diameter calculation.

The height of each stage, the diameter of the column, the number of rotations, the thickness of the rotor and stator and the shaft diameter was tweaked until reasonable numbers were obtained, using excel. The flows of both the phases were obtained from the extraction results in Aspen Plus. The standard ratio for the rotor diameter D_R , stator opening D_S and the column diameter is D_C is as follows: $D_R/D_C = 0.6$ and $D_S/D_C = 0.7$, which was assumed to be true for this system to reduce the number of factors (Chen, Sun, Song, & Yu, 2017).

The thickness of the rotors, stators, and the shaft, together with the other dimensions of the tower was needed to determine the void fraction of the column, which was required to calculate the residence time. In general, the increase of the volume of the shaft, stators and rotors meant an increase in pressure drop, therefore these values should be as small as possible. No sources were found that determine these values, so it was assumed that stators and rotors of 2 cm thickness and a shaft diameter of 10 cm still provided enough mechanical integrity.

Lastly, the real velocity of the continuous phase, u_c , was used as the average velocity required for the mechanical energy balance, where it was only required to calculate $E_{\rm fr}$. Using the dispersed phase velocity or the average of the two, showed little to no change in the overall pressure drop. Most of the pressure drop is because of the height of the tower.

It was found that the dispersed phase hold-up was heavily dependent on the rotor speed, where increasing the speed drastically decreased the dispersed phase hold-up. Furthermore, increasing the rotor speed reduced the droplet size, which normally reduces their drop velocity, causing flooding (S. A. F. Onink, 2011). Because of the decrease in drop size at higher rotor speeds, the hold-up should also increase, because of their slower drop velocity (Kung & Beckmann, 1961; Sharker, Phillips, & Mumford, 1985), however, this is not the case for an ionic liquid system in an RDC (F. Onink, Drumm, Meindersma, Bart, & de Haan, 2010). (F. Onink et al., 2010) explains it as follows: at low rotational speeds, the droplets tend to cohere together at the stator rings. When the rotor speed is increased the droplets start falling through the column at increasing speed, with increasing rotor speed. At sufficiently high rotor speed the hold-up should again start increasing with increased rotor speed, however, this was not observed in this thesis (S. A. F. Onink, 2011).

Lastly, the top and bottom settler of the column, see Figure 31, was assumed to be a stage without any internals. These parts are not used in any of the other calculations. Values of Table 38 only refer to the extraction section and the settlers. The final tower has a total height of 8.4 m and a pressure drop of 0.66 bar. In the Aspen Plus model, the top and the bottom settler pressure change is modelled as a valve and pump unit operation, named PDROPTOP and PDROPBOT, respectively.

It was found that the [EMIM][MeSO₃]-system and [EIM][NO₃]-system are very similar. It is possible to use the same tower for both cases, without any great differences. The only differences are the velocities, and then especially the ionic liquid-phase, the interfacial area, and the droplet size. The great similarity could be due to the calculations favouring the continuous phase, which was the fuel. Since the fuel stream is the same for both systems, no great differences should be present if this is the case.



Figure 31 extraction column

Distillation column design

Setup

In the process design of the distillation column, Aspen Plus is used for its entirety. Throughout the design process the same properties and NRTL method, as mentioned before, are used.

When designing a column an important factor is the pressure of the column. In general, the pressure should be as such that the dew point of the distillate is above 40°C to 52°C (Luyben, 2013b; Sinnott & Towler, 2013e). Where 40°C to 52°C is the temperature which can be reached in the cooler, using cooling water, which is typically available around 30°C (Luyben, 2013b). If too high pressure is needed to achieve this goal, refrigerants should be considered (Sinnott & Towler, 2013e). If the distillate has a very high boiling point or if heat-sensitive materials are distilled, vacuum operation is required, again the 40°C to 52°C distillate should be reached (Sinnott & Towler, 2013e).

Because the temperature in the reflux drum is known, namely at least 40°C to 52°C, the pressure of the reflux drum is also known, which is the vapour pressure of the reflux. The feed pressure should be slightly higher than this to account for the pressure drops over the trays, where 0.0069 bar is a good initial guess as pressure drop, per tray (Luyben, 2013b). When the condenser is specified to operate at 0.2 bar for the [EMIM][MeSO₃]-system and 0.15 bar for the [EIM][NO₃]-system, a temperature of 40°C for the distillate is reached. At a condenser pressure of 1 bar, the top stream temperature is 84°C for the [EMIM][MeSO₃]-system and 92°C for the [EIM][NO₃]-system. These options are also explored.

The optimum reflux ratio can be assumed by 1.15 times the minimum reflux ratio, however, this is a rough estimate (Sinnott & Towler, 2013e). Unfortunately, using this gives an unrealistic number of stages (166), which is due to the very low reflux ratio due to the small distillate stream. Because of this, the number of stages is assumed instead of the reflux ratio, for the DSTWU model. In the end, distillation is always a trade-off between energy input and the number of trays the column requires (Luyben, 2013a).

The number of stages of the tower was determined by using the simpler Aspen Plus unit operations, namely the DSTWU and Distl. These models apply the Winn-Underwood-Gilliland method and the Edmister method, respectively. Here the DSTWU model was first used and the results were checked using the Distl model. When these results were the same the RadFrac model was used, which is a far more powerful model, which is more prone to wrong input, and capable of sizing (Aspen Plus, n.d.-d).

The DSTWU requires the number of stages or reflux ratio as input, which are related to each other using the Gilliland correlation (Aspen Plus, n.d.-c). Furthermore, it requires the condenser and reboiler pressure, the condenser specifications (total, partial with all vapour, partial with vapour and liquid distillate) and the key component recoveries, where ideally the light key is equal to 1 and the heavy key is almost 0. Moreover, the DSTWU model also calculates the minimum number of stages using the Winn method and the minimum reflux ratio using the Underwood method (Aspen Plus, n.d.-c). Lastly, the DSTWU also gives the feed location as well as the reboiler and condenser duties (Aspen Plus, n.d.-c).

The Distl model requires way more input than the DSTWU model, namely the number of stages, the feed stage, the reflux ratio, the distillate to feed mole ratio, the condenser type, the condenser pressure and the reboiler pressure (Aspen Plus, n.d.-b). Everything that was obtained from the DSTWU model was entered here. The distillate to feed mole ratio was calculated by dividing the amount of required distillate by the amount of flow into the column, to get a rough estimate, since the value that is used in Aspen is slightly different. As mentioned, this model was used to check the results of the

DSTWU unit operation, before proceeding to the final model: the RadFrac. The RadFrac is a far more extensive model that allows for sizing and the calculation of pressure drop.

Distillation feed temperature

The feed temperature can be regulated using a pre-heater. A few considerations are important when deciding if this is a valuable asset for the column: energy efficiency and energy cost (C. L. Smith, 2012). Firstly, a pre-heater can prove to be more energy-efficient, if the required reboiler duty goes down, for the same amount of purity of the product (Lee & Binkley, 2011). However, if the temperature is too high, the heavy components are flashed at the feed stage, requiring more reflux to obtain the same amount of purity of the distillate. This increased reflux ratio, in turn, requires a higher boil-up ratio (Lee & Binkley, 2011). Sensitivity analysis is required to find the most energy-efficient feed temperature of the system (Lee & Binkley, 2011).

Sensitivity analysis was performed in a model using a DSTWU unit operation for the distillation. A preheater was used and a pump, which is set to 0.2 bar for the [EMIM][MeSO₃]-system and 0.15 bar for the [EIM][NO₃]-system, similarly to the pressure in the condenser and the reboiler of the distillation column. The feed is the same as the outflow of the extraction column bottom flow. An overview is given in Figure 32.



Figure 32 setup for sensitivity analysis for preheater specifications

To check if the use of a preheater is energy efficient, sensitivity analysis was performed. In this analysis the preheater temperature was varied and the duty of the preheater and the distillation column's reboiler is calculated. In Figure 33 the results are shown for the [EMIM][MeSO₃] system. Here it can be seen that the preheater duty increases, which is a logical consequence of the increased set temperature. The reboiler duty decreased with increasing feed temperature, where it intersects the preheater duty line around 200-205°C. The net duty remains constant. In terms of energy efficiency, there is no necessity for a preheater since no optimum temperature is available. This is true for both ionic liquids.



Figure 33 duty of the reboiler and the preheater as obtained by Aspen Plus sensitivity analysis, for [EMIM][MeSO₃]. The same shape is obtained for [EIM][NO₃].

Secondly, the energy cost is considered. For heating, steam is used, with some specifications of high, medium, and low-pressure steam shown in Table 51, in appendix J. Because of the high reboiler temperature, high-pressure steam is required. For the preheater medium pressure steam is used for a feed temperature up to 300°C and high-pressure steam from 300°C to 400°C. Aspen Plus also has a utility option for the simple heater models, however, the inlet and outlet temperatures of steam are 250-249, 175-174 and 125-124°C, with a pressure of 39.4, 8.76 and 2.32 bar for higher, medium, and low-pressure steam, respectively. This would mean that steam would not be a possibility for the reboiler, meaning that a fired heater is required, according to Aspen Plus. A superheated high, medium and low-pressure steam utility variable were added to the program, using the utility cost, temperature and pressure as shown in Table 51. All other values were copied from the Aspen Plus steam variant. (Sinnott & Towler, 2013g) calculated the cost of high-pressure steam (\$/Mlb) and subtracted the shaft work credit, which they calculated from the isentropic delta enthalpy and the steam turbine efficiency (0.85), to reach obtain an estimate for the cost of medium pressure and low-pressure steam. Hot oil and a fired heater are also considered for the pre-heater.

Since the [EMIM][MeSO₃] process at 1 bar has a reboiler temperature of 400°C, even hotter steam is required, as already shown in Table 51. For this superheated steam of 50 bar and 500°C was assumed and the shaft cost was calculated and added to the cost of 400°C, 40 bar steam, to get an estimate of the cost. The specific enthalpy of 500°C 50 bar steam is 3433 kJ/kg (TLV, 2020). A steam cost of \$7.65/Mlb was obtained using the same method as used in (Sinnott & Towler, 2013g).

To measure the utility for the reboiler using the DSTWU model, two heaters were added, one to cool the bottom stream back to the temperature it was before the reboiler and the second one to heat it back up. The utility of the second heater was measured. For the reboiler heating superheated high-pressure steam is used, with the inlet at 400°C and the outlet temperature 10°C above the outlet temperature of the reboiler, this is to avoid temperature crossing. Superheated low-pressure steam is not considered for the pre-heater or shown in the figures, because of the ridiculous streams required, generating cost of upwards of 16000 \$/h, greatly skewing the axis.

As can be seen from Figure 34 the total cost reduces with increasing feed temperature, this is because superheated high-pressure steam used for the boiler, is far more expensive than the other ways of heating. The brown line (superheated high-pressure steam) is straight because the reboiler uses it as well as the preheater, and it is known that the total duty of the two is constant. It should be noted that this figure only gives a general indication of the cost and should not be used as a direct quote, due to the simple model used. To conclude, increasing the feed temperature using cheap heating sources, is cost-effective. This is true for both ionic liquids.



Figure 34 total duty cost vs. preheater temperature at 0.2 bar, for [EMIM][MeSO₃] (similar curves for [EIM][NO₃]-0.15 bar)

Economizer

An economizer setup was also considered. In this setup, the heat of the bottom flow is used to heat the feed stream of the column, see Figure 35 (C. L. Smith, 2012). The goal of this setup is to reduce the reboiler duty as much as possible. This setup is simulated using the DSTWU unit operation as distillation column and a the heatx model (two-stream counter-current heat exchanger) for the economizer. Sensitivity analysis of this setup was performed and the heat exchanger area and reboiler duty vs. distillation feed temperature was obtained, as shown in Figure 36 for [EMIM][MeSO₃]. The minimum duty, with reasonable heat exchanger area, is obtained at a feed temperature of 280°C, which requires a heat exchanger area of 77.6 m² and a reboiler duty of 683 kW for [EMIM][MeSO₃]. for [EIM][NO₃] and the processes on atmospheric pressure, similar curves are obtained, however, the required heat exchanger area are (much) higher, although it is not unreasonably high. Furthermore, the simple calculation of Aspen Plus has far different results than the results as obtained from the geometry calculations and therefore the previously mentioned area should not be quoted as a fact.

Since no duty for the pre-heater is required, the total heat duty is greatly reduced. Therefore, it is decided to use this setup. This setup is worked out in more detail at the decided temperature, using a RadFrac model instead of a DSTWU, as well as a sized heat exchanger. All temperatures are at the intersect of the reboiler duty and heat exchanger lines, due to the exponential shape of the area curve. The temperatures are reported in Table 39.



Figure 35 Economizer setup for a distillation column with a preheater and reboiler (C. L. Smith, 2012)



Figure 36 analysis using economizer setup for [EMIM][MeSO₃], curves look similar for other systems

Final Aspen Plus model

Distillation column

Now that the design strategy is decided as well as the setup the full distillation part can be designed using a sized heat exchanger as an economizer. The final distillation column was designed using a sized RadFrac. As explained the DSTWU and Distl model was configured first before moving on to the RadFrac, where the results of the DSTWU and Distl were used.

When designing the trays of a RadFrac in Aspen Plus from scratch, a good approach is to start with the simplest model, as is learned from experience. In this case, the easiest was to first have the RadFrac run without any sizing at all and then gradually move on to Tray Sizing and subsequently Tray Rating. The results of the Tray Sizing could then be used as a first estimate in the Tray Rating step. Tray Rating was necessary because it supplies with more accurate and extensive dimensions of the column, as well as a pressure profile in the column.

Since vapour flow is very low due to the ionic liquid, bubble-cap plates were used in the column. Bubble-cap plates consist of risers with a cap on the top, with the cap containing holes on the edge to allow for flow (Sinnott & Towler, 2013e). Because of the risers, there is always liquid on the plates, which is not the case for other types of plates, which rely on high vapour flow to keep the liquid on the plates (Sinnott & Towler, 2013e). Bubble-cap is more prone to fouling, corrosion, plugging and are more expensive than more modern plate types (Sinnott & Towler, 2013e).

A variety of important tray dimensions is shown in Figure 37. Tray sizing requires the following specifications: tray type, number of stages, number of passes, tray spacing (default 0.6069), cap slot area to active area ratio (default 0.12). Tray sizing also requires some design criteria mostly related to foaming, overdesign and flooding, which was all left on default, only the flooding calculation method was entered, where Fair72's method was used. This is an updated version of Fair's method. The results obtained from tray sizing was the diameter, the downcomer width and side weir length. Of all these results only the diameter and downcomer width was used. Aspen Plus determined these dimensions for every tray.

The second step in determining the dimensions was the tray rating, where Aspen Plus checks the results based on flooding and downcomer back-up, which may not exceed 80% in Aspen Plus default settings. Flooding is when the liquid flows upwards in the column due to too high vapour velocity, which is in turn related to a too small tower diameter (Sinnott & Towler, 2013e). Downcomer back-up occurs when the amount of liquid and froth in the downcomer is too high, causing it to flow back onto the tray (Sinnott & Towler, 2013e). When designing the trays of the tower, one of the optional input values was the weir height. For vacuum operation the recommended length is 6 to 12 mm (Sinnott & Towler, 2013e), unfortunately, the minimum length in Aspen Plus is 10 mm. Another optional input is the downcomer clearance, which is typically 5 to 10 mm below the weir height, where a too low downcomer clearance can cause resistance to the flow and therefore downcomer back-up (Sinnott & Towler, 2013e). The downcomer was assumed to have the same width at the top and bottom. The last optional input that the tray rating allows to do is the layout and dimensions of the bubble caps. The default cap diameter for towers over 1.4 meters is 4" and the pitch is between 1.25" to half of the path flow length, which can be obtained from the previous tray sizing (Kooijman & Taylor, 2000). (Ludwig, 1997) recommends using a distance of 1.5" when using a cap diameter of 4". Since all optional input was used a much more accurate reflection of the pressure drop was obtained.

The final distillation column design for the distillation is shown in Table 39, which also contains important input from Aspen Plus. The table can be found in appendix G4. Furthermore, the obtained temperature and pressure profile is shown in Figure 48 and Figure 49, which can also be found in

appendix G4 and show an expected shape. It is important to note that in Aspen Plus, the top stage is stage 1 and is also the condenser, and the bottom stage is also the reboiler. Now that the column height is known, the pressure drop over the condensing stage can be calculated and consequently the power of the pump, which is required to pump the liquid from the condenser (which is on ground level) back up to the top of the tower. The pressure drop over the pipe back up was calculated using a simple Bernoulli equation with the stream size being obtained from the reflux rate.

As stated, the design was done for a vacuum and atmospheric setup. It is immediately evident when comparing the two regimes that the atmospheric distillation requires far more stages. Also, it can be seen that the reboiler has a very high utility cost, this is due to a large amount of high-pressure steam required, due to the high boiling point of ionic liquids.



Figure 37 tray dimensions based on pictures and descriptions in (Sinnott & Towler, 2013e)

Economizer

After the completion of the distillation column the preheater was sized, this way the pressure drop can be determined, which is required to determine the power the pump requires. During this process, a heater and pump unit operation block was present to maintain the temperature of the distillation feed at the correct temperature and pressure. This was necessary because changing the more extensive heatx model influences the feed stream temperature and pressure, which can cause errors in the loop. When the 'fake' heater and pump show a work of 0, the heat exchanger was correct, and the pressure drop is accounted for correctly.

First, a heat exchanger type must be chosen, using TEMA designations. Because of the high temperature increase (25°C to 280°C), a simple BEM type exchanger cannot be used (Sinnott & Towler, 2013b). Exchangers with an internal floating head allow for high temperature difference, therefore this type is used (Sinnott & Towler, 2013b). It is important to note that these type of heat exchanger require an extra-large shell to allow room for the floating head flange (Sinnott & Towler, 2013b).

The design in Aspen was done while using the heatx unit operation on simulation mode, i.e. the results of the heat exchanger are generated entirely on geometry. The simulation was first performed with no pressure drop and only heat transfer calculations, the so-called U methods. When the correct

temperature was obtained the pressure drop is also calculated from the geometry. Experience shows that this order improves the convergence during simulations. For the geometry the inside shell diameter and shell to bundle clearance was first decided upon, using standard values for the pull-through floating head systems (Sinnott & Towler, 2013b). It was also determined that the TEMA shell-type was F, a two-pass shell, with also two tube passes. This was required to obtain a high enough temperature. From there the number of tubes was determined using Equation 51. The tube size was assumed using standard sizes as given by (Sinnott & Towler, 2013b). The pitch was calculated by multiplying the outside tube diameter by 1.25 and a triangle pattern was used for improved heat transfer (Sinnott & Towler, 2013b). The length of the tubes was also assumed and adjusted to obtain the correct cold-out temperature. Copper tubes are used because a high amount of heat transfer is required. Lastly, the number of baffles, baffle cut, and nozzle diameters were assumed. Because the liquids going into the hot and cold side are approximately the same in size and the majority is ionic liquid, the nozzle diameters were assumed to be the same. The results are shown in Table 40, which can be found in appendix G5.

$$N_{Tubes} = K_1 \left(\frac{D_{bundle}}{D_{tube}}\right)^{n1}$$

Equation 51 number of tubes for a heat exchanger using the bundle diameter and outside tube diameter. K_1 is 0.249 and n1=2.207 for two tube passes. (Sinnott & Towler, 2013b)

PFD

The PFD applies to both the vacuum and atmospheric distillation process because the pump P2, is used to bring the liquid from vacuum to 2 bar in the vacuum process, and from 1.1 bar to 2 bar in the atmospheric process. This is because the pump is incorporated to overcome the pressure drop of E1, E4 and the height of the extraction column C1. Furthermore, the throttle valve that is present in front of the distillation column, is incorporated into the PFD, because of its necessity to reduce the pressure of the distillation feed. No other valves are present in the PFD.

The vacuum-process PFD is shown in Figure 38. The make-up of ionic liquid enters in stream 2 and is mixed with the recycled ionic liquid from stream 19. The ionic liquid enters the extraction column (C1) at the top in stream 3. In stream 1 the hydrocarbons enter the extraction column at the bottom of the tower. At the top of the extraction column thiophene poor hydrocarbon is released in stream 4 and at the bottom of the tower thiophene rich ionic liquid is released in stream 5. Stream 5 is heated in an economizer (E1) with the bottoms product (stream 17) of the distillation column (C2). The heated stream (6) enters the distillation column through a throttle valve (TV1), to reduce the pressure to vacuum conditions in the vacuum processes or around 1.0 bar for the atmospheric process, from 1.6 bar. At the top of the distillation column, the distillate is cooled (E2) and the mixture of liquid and vapour is collected in the reflux drum (V1). The reflux is pumped back into the distillation column (stream 12, pump P1) and the distillate is in stream 13. Stream 13 contains a mixture of ionic liquid, thiophene, n-heptane and n-octane and is considered waste. The heat exchanger is cooled using cooling water (stream 20). The bottom stream (14) passes through a reboiler (E3). The reboiler is heated using high-pressure steam (stream 22). The vapour of the reboiler is fed back to the distillation column in stream 15 and the bottoms product (stream 16) is fed to the pump P2, which increases the pressure to about 2 bar pressure, to overcome the pressure drop of E1, E4 and the height of C1. Stream 16 contains pure ionic liquid. After the pump, stream 17 leads the hot ionic liquid to the economizer (E1) where it cools down and heats stream 5. The cooled down ionic liquid in stream 18 is further cooled down back to 25°C in E4, which runs on cooling water (stream 24). The subsequent stream 19 completes the recycling of ionic liquid. An overview of Figure 38 is shown in Table 6.



Figure 38 process flow diagram process.

Table 6 Annotations for the PFD

Unit operation	Code	Purpose
Extraction column	C1	Extraction of thiophene from the hydrocarbons (1) using ionic
		liquid (3).
Distillation column	C2	Separation of the ionic liquids (16) from the other components
		(13).
Economizer	E1	Heating the distillation feed (6) using the C2 bottom stream (17).
Condenser	E2	Cooling of the top gas (8) of the C2. Utility: cooling water.
Reboiler	E3	Boiling up the bottom liquid (14) of the C2. Utility: high-pressure
		steam.
Cooler	E4	Cooling stream 18 back to 25°C. Utility: cooling water.
Throttle valve	TV1	Reducing the pressure of the distillation column feed (7).
Condenser pump	P1	Pumping the reflux and distillate from ground level back into the
		C2 (11).
Pre-economizer pump	P2	Increasing the pressure drop of ionic liquid to overcome the
		pressure drop over E1, E4 and the pipe to the top of C1.
Reflux drum	V1	collection of condensed top liquid of C2.



Figure 39 Piping and instrumentation diagram

Annotation	Definition	Explanation
F	Flow rate	x
FF	Flow ratio	x
Р	Pressure	x
Т	Temperature	x
L	Level	x
хт	x Transmitter	Transmits the value of x over the stream or inside equipment.
xIC	x Indicating Controller	Displays value of x transmitted by the xT and controls the valve.
xV	x Valve	Valve controlled by the xIC. The final control element
хРР	x Pump	Pump controlled by xIC. The final control element
Circle without bar	Field mounted instrument	This piece of equipment is present outside of the control room.
Circle with bar	Panel mounted instrument	This piece of equipment is present inside the control room.
TV	Throttle valve	The throttle valve is a butterfly valve.
V	Valve	Normal valve or pressure relief valve (V-4)
Striped line	Electric signal	The transmitting between these pieces of equipment is done using an electric signal.
Line with circles	Software signal	Software between two different indicating controllers, connected to one single final control element.
Two vertical lines	Restriction orifice	Used to measure the flow rate over a stream. Connected to an FT.

Table 7 Annotations used in the P&ID (Sinnott & Towler, 2013c)

The P&ID shown in Figure 39, is based on the PFD shown in Figure 38. The equipment annotations are the same. The explanation of the extra annotation (valves, FT, FIC, FV, etc.) in the P&ID is shown in Table 7. (Sinnott & Towler, 2013c) was the main resource for the design of the P&ID. Control over every piece of equipment is discussed separately. The stream numbers are the same as in the PFD, however, they have been segmented. For example stream 3 is 3_1, 3_2 and 3_3.

Firstly, pump P3 is used to control the amount of make-up ionic liquid that should be present in stream 3. This is done by passing the liquid through a restriction orifice, connected to a flow transmitter, FT. This flow transmitter signals the flow indicating controller (FIC), which in turn slows down or increases the number of rotations of the pump, the final control element (FPP) in stream 2. This is to ensure that when more or less ionic liquid is recycled in 19, the correct amount is still added.

Secondly, the extraction column (C1) is discussed. The column is controlled using the top flow because this is the flow where our product is (thiophene poor n-heptane/n-octane). This flow is controlled using V-2, which is present in stream 26. It is not possible to implement this valve in stream 3, because the ionic liquid needs to go somewhere, which is tank T1, from where also the make-up ionic liquid is provided. At the bottom, the hydrocarbon inlet (1), is only controlled for the correct amount of flow, through V-1. Furthermore, whenever a liquid-liquid or liquid-vapour layer is present, a level controller should be present (Sinnott & Towler, 2013c). These level controllers (LT, LIC) are connected to V-4 (LV) for the top settler and V-5 for the bottom settler. Lastly, the column has a pressure relieve valve (V-3) in case of overpressure due to too much hydrocarbon.

The next piece of equipment is the economizer (E1). Since this is a counter-current heat exchanger that employs the bottom stream of C2 for its hot side, instead of high-pressure steam, no control is possible. The only thing that is added is a control room mounted temperature indicator (TI), for troubleshooting.

To regulate the feed pressure of the distillation column (C2), a throttle valve (TV1) is installed between stream 6 and 7, which is regulated using a pressure transmitter (PT) and pressure indicating controller (PIC). This butterfly valve can close further in the case of too high pressure in 7 and open wider in the case of too low pressure.

The distillation column (C2) of course contain a liquid-vapour layer which is present in the bottom of the column and the reflux drum (V1), which has to be controlled (Sinnott & Towler, 2013c). This liquid level is controlled using level controllers connected to the top distillate valve V-7 for the top of the tower. The liquid level at the bottom of the tower is controlled by valve V-10 in stream 14, to ensure that more or less bottom product is obtained. The pressure in the column is controlled using the condenser (E2) which is done using a pressure controller in steam 8, connected to the cooling water valve, V-6. Since the goal of the distillation column is to obtain pure ionic liquid for recycling, the bottoms product is more important than the top. When the bottom product is more important, the temperature of the column is controlled using the bottom of the tower (Sinnott & Towler, 2013c). When the temperature in the column drops, which would be due to too little ionic liquid, V-9 is closed by the temperature controller, decreasing the reboiler duty. This means that the reflux is controlled using a simple flow ratio controller connected to V-8, which makes sure that the correct reflux to feed flow ratio is obtained for the process. In the reboiler, the liquid level on the left-hand side of the overflow baffle is controlled by pump P2, which also takes the pressure drop of the tower into account. It does so by combining the PIC and LIC with a software link.

Lastly, the cooler (E4) is controlled by measuring the temperature after the cooler in stream 18 and supplementing the amount of cooling water accordingly using V-11. Since cooler might have issues with scaling, reducing the cooling abilities, the temperature controller has to be placed after the exchanger.

Mass balance

The mass balances are obtained from the finished Aspen Plus models and are presented in appendix H. It is assumed that when the process runs accordingly, stream 26 is empty, hence the N.A. in the mass balance.

As shown in the balances, the n-heptane and n-octane layers only have 10 ppm. Since the ionic liquid is recycled, only a small amount of make-up is required, which is the ionic liquid that is lost in the condensing stream. As can be seen from Table 8 all of these flow rates are almost negligible, compared to the total extraction feed.

Table 8 flow rate of lost ionic liquid and the percentage loss of the total feed (20070 kg/h [EMIM][MeSO₃] and 26027 kg/h for $[EIM][NO_3]$)

Process	Φ _m (kg/h) make-up	Percentage lost
[EMIM][MeSO ₃] vacuum	0.215	0.001%
[EMIM][MeSO ₃] atmospheric	0.053	0.0003%
[EIM][NO ₃] vacuum	0.053	0.0002%
[EIM][NO ₃] atmospheric	0.342	0.001%

Another major observation from the mass balances is the required utility for the reboilers. Especially the atmospheric [EMIM][MeSO₃]-process requires more high-pressure steam than its vacuum counterpart. Furthermore, hotter steam is required, which is, later on, be reflected in the economic analysis. For the [EIM][NO₃]-process the utility flows of the reboiler are almost the same, however, the atmospheric process requires hotter steam. The same observations can be made for the cooling water utility of E4, which is again higher for the atmospheric processes, with the [EMIM][MeSO₃]-process having the biggest increase.

Heat balance

For the required pumping power of P2 and the pressure drop over TV2, the pressure drop over the cooler E4, is required. To calculate this pressure drop the overall heat transfer coefficient U was copied from the results of the economizer and implemented into an Aspen Plus Heatx model. From this, the required heat transfer area was calculated by Aspen, which can be related to the pressure drop and the heat exchanger area of the economizer (1:1). The results are shown in Table 49, in appendix I. The pressure drop over the economizer E1 is already known. Note, the pressure required to pump the ionic liquid to the top of C1 is also supplemented by P1 and is calculated by a simple Bernoulli equation. For the [EMIM][MeSO₃]-process this drop is 0.938 bar and for the [EIM][NO₃]-process this drop is 0.944 bar.

The heat balance for both the vacuum and atmospheric processes of both the ionic liquids is shown in Table 9, together with their required utility input. Note that the duty of the economizer (E1) is the heat that is exchanged between the two phases. The size of the utility streams, as well as the cost of the streams, is shown in the mass balance and economic analysis sections, respectively. As can be seen from Table 9 the major energy contributions are from the heat exchangers E3 and E4.

Lastly, for the modelling of the condenser of the reboiler, for subsequent economic analysis, the area is required. This value was obtained using Equation 52 since Q and the temperature differences are known and the logarithmic mean temperature difference, ΔT_m , can be calculated. Furthermore, an overall heat transfer coefficient of U=700 W/m².K can be assumed for a condenser cooling organics using water (Sinnott & Towler, 2013b). The temperatures are shown in the mass balances and the duty is shown in Table 9. The area of the reboiler was obtained using the same method, with an assumed U of 500 W/m².K. The obtained areas are depicted in Table 50, in appendix I. The heat exchanger area for the cooler (E4) was obtained from Aspen Plus and is shown in Table 49. For the economizer (E1), the results as shown in Table 40, which can be found in appendix I and G5 respectively.

$$Q = UA\Delta T_m = UA * \frac{\left(T_{hot,in} - T_{cold,out}\right) - \left(T_{hot,out} - T_{cold,in}\right)}{\ln\left(\frac{T_{hot,in} - T_{cold,out}}{T_{hot,out} - T_{cold,in}}\right)}$$

Equation 52 Heat transfer in a heat exchanger, with U the heat transfer coefficient in W/m^2 .K and A the area (Sinnott & Towler, 2013b)

Equipment duty (kW)	Utility type	[EMIM][MeSO₃]	[EIM][NO₃]	[EMIM][MeSO₃]	[EIM][NO₃]
Operating	N.A.	Vacuum		Atmospheric	
Tegime Cz					
C1	Electric	1.7	1.7	1.7	1.7
E1	N.A.	3238	4719	4423	6388
E2	Cooling	-19.5	-16.8	-14.8	-21.8
	water				
E3	High	972	995	1767	1198
	pressure				
	steam				
E4	Cooling	-954	-981	-1756	-1176
	water				
P1	Electric	0.70*10 ⁻³	3.55*10 ⁻³	1.47*10 ⁻³	2.66*10 ⁻³
P2	Electric	1.51	2.09	0.77	1.03

Table 9 Duty of the different equipment pieces for all four different processes

Economic analysis

The utility cost of cooling water and electricity is $2.17*10^{-7}$ \$/kJ and 0.0775 \$/kWh, respectively, as specified by Aspen Plus. The water cost is specified to be around 0.02\$/1000 gal by (Sinnott & Towler, 2013g). If stream 24 is taken as an example and the utility cost of E4 as specified in appendix J, the cost can be calculated to be 0.017 \$/1000 gal, which means that the value as specified by Aspen Plus is correct. The electricity cost is around 0.06\$/kWh as specified by (Sinnott & Towler, 2013g), so it can be assumed that the cost as defined by Aspen Plus is probably roughly correct. The high-pressure steam cost was defined earlier. The costs of all the different required utilities for the equipment pieces are shown in Table 52, which can be found in appendix J, for all the four different processes.

The equipment cost was obtained from Aspen Economical Analysis. These costs were subsequently multiplied with Hand's Installation factor to account for all the piping, valves etc. (Sinnott & Towler, 2013a). The results are shown in Table 53, which can be found in appendix J and includes the installation factor.

The extraction column (C1) was modelled as a trayed tower, without any trays. 12 theoretical trays are chosen to account for the bottom and top settler. The spinning discs were modelled as 10 different 'sanitary high-shear homogenizing agitators', with the rotator stator impeller type. Both the tower and impellers are made from carbon steel because it suits the operating conditions and it is relatively cheap (Sinnott & Towler, 2013d).

The vacuum distillation column (C2) was modelled as a simple carbon steel trayed tower, using bubble cap trays. Reboiler and condenser equipment is modelled separately. The atmospheric processes require SS304 in the economic analysis, due to the temperature limit being reached for carbon steel. The condenser (E2) was assumed to be a BEM type heat exchanger, with the area as mentioned in the heat balance section for the vacuum processes. For the atmospheric processes, the calculated area was too small, therefore the smallest possible area is assumed, which is 0.33 m². Carbon steel was again assumed. The reboiler was modelled using a standard reboiler model, with the area as mentioned in the heat balance section. Carbon steel was again assumed.

The cooler (E4) was modelled as a floating head heat exchanger, similarly to the economizer, and for the same reasons: the high temperature difference (Sinnott & Towler, 2013b). The area is shown in

the heat exchanger section and the tubes were assumed to copper, because of the high amount of heat transfer required. The shell was assumed to be carbon steel.

The reflux drum (V1) requires a size as input. From Aspen Plus it was obtained that the liquid flow rate is about 0.2 m^3/h . Assuming that residence time of the drum is about 10 minutes, the drum liquid volume can be calculated to be 0.03 m^3 , which was assumed for all four cases. Again carbon steel was assumed.

The pumps only require the liquid flow rate as required input, which was obtained from the mass balance using the density from Aspen Plus. The duty of the pump was also implemented into the economical analyser. Since the duty and flow over P3 is unknown, it was assumed that it costs the same as P2. Since the make-up stream is very low, the utility can be assumed to be negligible, however, the pump needs to be capable to handle a large stream, if the recycle fails.

Lastly, the tank (T1) was assumed to be a simple vertical tank of 20 m³, which should provide more than enough back-up ionic liquid for the process. The material of this tank is aluminium because it is cheap and lightweight (Sinnott & Towler, 2013d).

To obtain a return of investment of the equipment, an operational time of 10 years and 8000 hours operational hours per year was assumed, this yields an hourly cost of the equipment. Using the results of both the utility and the hourly equipment cost, the total costs can be calculated and are shown in Table 10. It can be seen that the vacuum-operated [EIM][NO₃]-process is the cheapest.

Hourly cost	[EMIM][MeSO ₃]	[EIM][NO ₃]	[EMIM][MeSO₃]	[EIM][NO ₃]
Operating	Vacuum		Atmospheric	
regime C2				
Equipment (\$/h)	38.51	62.18	45.09	58.89
Utilities (\$/h)	315.88	189.69	509.93	222.52
Total (\$/h)	354.39	251.87	555.02	281.41

Table 10 Total hourly cost

Comparison between ionic liquids and operation conditions

With the process design and simulation completed a comparison between the ionic liquids can be made. Furthermore, a comparison between the vacuum-distillation or atmospheric distillation is made in this section.

Using Aspen Plus, it was determined that the followings feeds are required: $[EMIM][MeSO_3]$ 20070 kg/h and $[EIM][NO_3]$ 26027 kg/h. They both have the same number of 10 stages. Furthermore, since the RDC that was designed can be used for both ionic liquids, $[EMIM][MeSO_3]$ is the preferred choice from an extraction perspective. This was also already seen in previous sections, namely both the screening of ionic liquids and the results of the experimental results, where it was shown that $[EMIM][MeSO_3]$ has a higher selectivity.

Secondly, the separation section, where the ionic liquid is heated up using the bottom stream of the subsequent distillation tower's reboiler. When comparing the vacuum operation and the atmospheric operation, it can be seen that atmospheric distillation requires significantly more stages. Furthermore, it can be seen that a significantly higher reboiler duty is required for atmospheric distillation, due to the increased boiling point. This gives the atmospheric process significantly higher reboiler duty cost, especially for the [EMIM][MeSO₃] process, see Table 52 in appendix J. Moreover, not only do the

vacuum processes require more expensive steam, but they also require more flow, as can be seen when comparing the mass balances.

However, the required heat transfer area of the economizer is lower when the operation is performed at atmospheric pressure, which is due to the higher ΔT_m , which acts as the driving force of the heat exchanger. The duty of E1 is increased, however. This is due to the higher output temperature, compared to the vacuum process. A comparison of the heat exchanger costs show that the economizers of the atmospheric operation are cheaper, see Table 53 in appendix J.

Although the mass flow of the ionic liquid stream for [EMIM][MeSO₃] is roughly 77% of the [EIM][NO₃], the reboiler duty of both are roughly equal to each other in the vacuum process, both approximately 1.0 MW, see Table 39 in appendix G4. However, the reboiler utility requirement of [EIM][NO₃] is significantly lower as is shown from the mass balance and is reflected by the cost as shown in Table 52 in appendix J. Since the boiling point of [EIM][NO₃] is lower than [EMIM][MeSO₃], the reboiler utility is decreased. The heat duty is equal for both cases, because [EIM][NO₃] has a higher heat capacity, as shown in appendix E.

The economizer for the [EIM][NO₃] is significantly larger, however, which yields a twice as expensive heat exchanger. This is since more heat is exchanged between the hot and cold side for the [EIM][NO₃] systems, due to its higher heat capacity. Note that the thermal conductivities of both ionic liquids are approximately equal to each other, as shown in appendix E. Also note that the ΔT_m for the [EIM][NO₃] economizer is lower than [EMIM][MeSO₃], indicating that the less heat should be transferred, i.e. lowering the duty. However, the significantly higher heat capacity of [EIM][NO₃] counteracts this, increasing the required duty exchanged, to reach the desired temperature.

When comparing the overall cost of the four different processes, it can be seen that the vacuum processes are cheaper than the atmospheric processes, which is especially the case for [EMIM][MeSO₃], as can be seen in Table 53. The overall cheapest process is the vacuum-operated [EIM][NO₃]-process.

Comparison between ionic liquids and sulfolane

To draw a comparison between the ionic liquids and sulfolane, a variety of comparisons is made. First, the overall process design is considered. Secondly, a comparison between mass balances is made. Thirdly, the heat of the reboiler, and in this thesis' case the economizer, is considered. It was already determined in the introduction that sulfolane has a higher ecotoxicity than either of the discussed ionic liquids.

Firstly, the overall process design. In the introduction, it was mentioned that the sulfolane process requires two distillation columns, whereas the ionic liquid process only requires one (Song et al., 2018). In the process design, it was determined that the ionic liquid indeed only require one distillation column, which is in line with other process designs (Abdulwahab, 2013; Larriba et al., 2018; Liu et al., 2020; Song et al., 2018). This makes the ionic liquid in terms of the required amount of process equipment, the better option.

No conclusion is drawn from the make-up, regarding the preferred ionic liquid. In the comparison of the ionic liquids with sulfolane, it is shown that lost amount of solvent is far larger for the sulfolane process, with their make-up stream being around 0.02% of the total stream (Song et al., 2018). The lost amount of ionic liquid in this work is about 50 to 100 times smaller, which is in line with the results regarding their tested ionic liquids (Song et al., 2018).

Next, the heat balance is discussed for both processes. Since the example sulfolane process used, uses no distillation feed pre-heater, nor do they report the energy requirement of cooling down the sulfolane, a comparison is made between heating streams only. For the sulfolane process, this is two different reboilers and for the ionic liquids, this is the reboiler and the economizer. The results are shown in Table 11. It is important to note here that the economizer requires no duty, however, if it was not present like in the case of (Song et al., 2018), this gives a rough estimate of the required reboiler duty. As can be seen from Table 11, sulfolane requires a total higher heat duty, than both ionic liquids in the vacuum distillation configuration. The atmospheric configuration, however, requires a higher heat duty, due to the higher boiling points. Alternatively, when the total feed of the extraction process is taken into account it can be seen that that sulfolane requires more duty per unit of mass feed, see Table 11.

Process	Total heating duty (kW)	Total feed (kg/h)	Total heating duty per kg feed (kW/kg)
Sulfolane	5882	23341	0.25
[EMIM][MeSO ₃] vacuum	4210	30070	0.14
[EIM][NO ₃] vacuum	5714	36027	0.16
[EMIM][MeSO ₃]	6190	30070	0.21
atmospheric			
[EIM][NO ₃] atmospheric	7586	36027	0.21

Table 11 Comparison between heating duties of different solvents, with sulfolane obtained from (Song et al., 2018).

Discussion

This thesis aimed to find a suitable alternative of sulfolane for the desulfurization of oils. For this process, the oil was modelled as n-heptane, n-octane and thiophene, making it a very simplistic model. Future studies are required to validate these ionic liquids with a more realistic model, which requires more similar experimental work to obtain the NRTL values for all the different components of oil.

Another aim of this thesis was to compare the two chosen ionic liquids with each other, for which two promising ionic liquids were chosen from a screening. Since the two best ionic liquids were picked and the comparison showed that the 'worse' one, in term of selectivity, had the better design results, future studies are needed to compare these ionic liquids to other ionic liquids. These other ionic liquids can have a lower performance index than [EMIM][MeSO₃] and [EIM][NO₃] but could have superior properties in terms of boiling point, viscosity, etc. A possibility could be to expand the Matlab code to also include the boiling point.

In the experimental work, it was determined that the conventional stirring method did not work for these ionic liquids, creating very unexpected results. Although it is unclear why exactly this is the case, it could be hypothesized that it was due to the very high viscosity differences of the liquids present in the flask. Because of the improper results, it was decided to switch to a shaking method, which is less used for these type of experiments. However, since the main goal of the shaking and stirring is to obtain proper mixing before equilibrating the mixture, the method of how to achieve this mixture is not an issue. As already mentioned in the experimental work, one experiment was repeated and shaken for 15 hours, which only showed a few per cent differences in the final results, meaning that the 6-hour shaking method indeed acquires proper mixing and reaching equilibrium after settling overnight.

When analysing the experimental results, slightly unexpected behaviour is observed for the selectivity and distribution graphs are obtained. Some points do not fall on the expected downward slope,

however, this is sometimes also observed in other works, as is shown in Figure 9 to Figure 12. It should be noted that other works have more data points than this work. It could be the case that the expected curve is more prominent if more points are added. Fewer points were considered, because there was no necessity for it, for the subsequent process design. It is expected that that at lower x_2^{HC} , the selectivity and distribution are higher, and at higher x_2^{HC} it is lower, something that is also already visible from the data points collected.

Moreover, the main goal of the experimental section was creating the tie-lines, from which the NRTL constants were regressed. The experimental tie-lines do show expected behaviour. Furthermore, the experimental results were also checked using mass balances and the Hand and Othmer-Tobias correlation, which all showed good results, meaning that the obtained tie-lines are correct. Lastly, it should be mentioned that the amount of tie-lines is this work (6), is lower than in most other works. However, since only a small amount of thiophene is present in fuel (x_2 <<0.5), this does not matter for the process design.

The H-NMR was used for quantitative analysis of the ionic liquid layers, which contained very small amounts of n-heptane and n-octane. This generated a very small peak for this particular component. Since the mole fractions were obtained from the normalized results, this very small peak, in combination with the normalization and human error, could prove to be very sensitive to errors. However, the n-heptane n-octane fractions in the ionic liquid layer are all in the same order of magnitude, which is to be expected and suggests the correctness of the results. Nevertheless, it is advised that for future experimentation a method similar to the internal standard of the GC is used.

The experimental results show a good correlation with the Matlab screening results. However, $[EIM][NO_3]$ was not considered in the screening since it was a replacement for $[EMIM][NO_3]$, therefore, no conclusions in regards to the screening can be drawn from this particular ionic liquid and its relation to either [DMIM][MP] and [BMIM][SCN].

Normally, when an extraction column is designed, a lab setup is used to study the behaviour and create a model from the results. This allows the designer to also study entrainment and flooding, amongst other things. Since no lab study was performed for the design of the RDC, the entire design was created using the work of (S. A. F. Onink, 2011), who also used ionic liquids. Using his formulas, a plausible design was created. It could be the case that this design is unsatisfactory in real-world applications and it should therefore first be recreated on a lab scale.

Of course, after removal of the thiophene, a solution has to be proposed for the thiophene destruction. The obtained thiophene is in a mixture with n-heptane, n-octane, and the ionic liquid. Flaring is a possibility, where the heat can be used in the ionic liquid extraction process or at another location of the refinery. It should be noted that the burning of this mixture should be done with the necessary clean-up methods, since sulphurous gasses are released, due to the presence of thiophene.

As stated in appendix E, many of the properties of [EMIM][MeSO₃] and all properties of [EIM][NO₃] are not experimental values but calculated by mainly group contribution methods. A large part of the process design is based on these calculated properties, which could have a huge influence on the conclusions that are drawn if they are wrong. This is especially the case for the boiling points, which played a major factor in the utility requirement. However, the statistical parameters of all the used literature are satisfactory, validifying the obtained results.

In the comparison of the ionic liquid with the sulfolane process, the process of (Song et al., 2018) is used as an example for sulfolane. It is important to note that their model fuel has a different make-up than the one n-heptane/n-octane/thiophene mixture in this thesis, which is modelled as a 50 wt%/50

wt%/520 ppm mixture. The model fuel of (Song et al., 2018) is a mixture of n-octane, toluene, cyclohexane and thiophene, with the mass fractions of 70 wt%, 15 wt%, 15wt% and 100 ppm respectively. The goal of their paper is to also obtain 10 ppm thiophene in the product, however, since they only start with 100 ppm, this makes a comparison of the extraction columns difficult.

Since sulfolane can be also be used for the denitrogenating of fuels, as discussed in the introduction, the ionic liquids proposed in this thesis should also have this quality if they are to replace sulfolane in the petrol industry, due to the variety of nitrogen compounds present in fuels (Abro et al., 2016). This means that further studies are required to examine this possibility. It has been reported that some ionic liquids possess this ability (Abro et al., 2016).

Moreover, in the comparison with sulfolane, no economic comparison could be made, due to limited information available in this respect. To determine if the ionic liquid process is cheaper than sulfolane a full economic analysis needs to be performed of the sulfolane process, which requires extensive research and design. However, due to the lower heat duty and the fact that only one distillation tower is required when using ionic liquids, it can be assumed that ionic liquids are probably a cheaper alternative.

Furthermore, a lot remains uncertain about the toxicity of ionic liquids, which was briefly discussed. Extensive research must be performed on the toxicity of [EMIM][MeSO₃] and [EIM][NO₃], before implementation on a larger scale. From current literature we learn that the proposed ionic liquids are less toxic than sulfolane, however, they remain far more toxic than thiophene.

Conclusion

Using the screening method in Matlab, which employed the infinite dilution activity coefficients, the two ionic liquids were chosen, based on their high-performance index. When comparing the selectivity and distribution results, with other ionic liquids, as shown in Figure 9 to Figure 12, it can be concluded that the screening method proved to be a viable option for choosing ionic liquids. This was concluded since the distribution and selectivity [EMIM][MeSO₃] had a similar relation to [BMIM][SCN] and [DMIM][MP] in both the experimental results and Matlab screening, as explained in the results section. Moreover, the selectivities of the chosen ionic liquids are indeed very high, as expected from the screening, further validifying the use of the screening method.

The experimental work was performed using the less conventional shaking method, where it was determined that shaking for 6 hours and settling overnight, indeed reaches an equilibrium situation, from where the tie-lines can be determined. The experimental results show that of all the ionic liquids, with available LLE data, [EMIM][MeSO₃] has the best selectivity for the n-octane system and is only outperformed by [DMIM][MP] for the n-heptane system. [EIM][NO₃] on the other hand, shows slightly worse, but still promising results, in terms of selectivity. The distribution of both ionic liquids is mediocre. The downward shape of the selectivity and distribution curves indicate that the ionic liquids are particularly useful at lower thiophene concentrations, which is the case in this thesis (only 520 ppm).

Although the selectivity and distribution graphs do not exactly fit a good curve, it can be determined that the results are correct, from the mass balance and the performed Hand and Othmer-Tobias correlations. Moreover, the obtained liquid-liquid equilibrium tie-lines that are depicted in the triangle plot are correct, which can be observed from the plot itself, where it is shown that no tie-lines intersect and the point on the right-hand side show a nice curve. The point on the left-hand side should, of course, be on the edge of the graph, because the ionic liquid fraction is 0.

The obtained tie-lines were properly regressed to NRTL data, where the NRTL and experimental tielines show good overlap. Moreover, the RMSD deviation is within bounds and the NRTL results are checked using an extensive method. It can confidently be stated that the obtained NRTL data is correct and provides with good process-design results.

In the process design, it was determined that [EMIM][MeSO₃] had the best extractive properties, which was expected from the initial screening. This meant that [EIM][NO₃] required a significantly larger flow rate. However, since almost all ionic liquid can be recycled, the better extractive ionic liquid is not the better ionic liquid overall. Mostly due to its lower boiling point, the utility cost of the [EIM][NO₃]-processes are far lower than [EMIM][MeSO₃]'s. This lower boiling point was also reflected in the cost when comparing the vacuum and atmospheric processes, where the atmospheric processes required more flow and more expensive steam, which was especially the case for [EMIM][MeSO₃]. Unfortunately, the equipment cost of the [EIM][NO₃]-processes is higher, due to its higher heat capacity requiring larger heat exchangers, which is a major factor of the overall equipment cost. However, when a return of investment of 80000 hours is assumed, the largest costs are from the utilities. Overall, it can be seen the [EIM][NO₃] vacuum process is cheaper than all other processes, making it the superior of the two ionic liquids if all ionic liquid is recycled.

In the comparison of the ionic liquids with sulfolane, it was determined that the proposed ionic liquids are indeed better than sulfolane, for the removal of thiophene. This is due to its better recyclability, the fact that only one distillation tower is required, and the heat duty required for the process is lower. Moreover, in the comparison with hydrotreating, it is shown that less severe temperature and pressure conditions are required.

To sum up, it was determined that of the two ionic liquids, that were chosen through a Matlab screening, $[EIM][NO_3]$ is the better option for the removal of thiophene from an n-heptane/n-octane mixture, which is mostly due to its lower boiling point. The only downsides of $[EIM][NO_3]$ were the higher amount of ionic liquid flow required, due to its lower selectivity compared to $[EMIM][MeSO_3]$ and the bigger heat exchanger required due to the higher heat capacity.

References

- Abdulwahab, M. (2013). Modelling of ionic liquids' thermal separation and recycling in biomass fractionation. Master's thesis. *Aalto University*, 77.
- Abro, R., Abro, M., Gao, S., Bhutto, A. W., Ali, Z. M., Shah, A., ... Yu, G. (2016). Extractive denitrogenation of fuel oils using ionic liquids: A review. *RSC Advances*, Vol. 6, pp. 93932–93946.
- Anantharaj, R., & Banerjee, T. (2013). Thermodynamic properties of 1-ETHYL-3-methylimidazolium methanesulphonate with aromatic sulphur, nitrogen compounds at T=298.15-323.15K and P=1bar. *Canadian Journal of Chemical Engineering*, *91*(2), 245–256.
- Asadollahzadeh, M., Shahhosseini, S., Torab-Mostaedi, M., & Ghaemi, A. (2016). Drop behavior in a pilot plant Oldshue-Rushton extraction column for three various liquid-liquid systems. *Separation and Purification Technology*, 159, 7–17.
- Aspen Plus. (n.d.-a). Aspen Plus Help: extract.
- Aspen Plus. (n.d.-b). Working with Distl.
- Aspen Plus. (n.d.-c). Working with DSTWU.
- Aspen Plus. (n.d.-d). Working with RadFrac.
- Beek, W. J., Muttzall, K. M. K., & Van Heuven, J. W. (2000a). Flow Phenomena. In *Transport phenomena* (2nd ed., pp. 68–76). Chichester.
- Beek, W. J., Muttzall, K. M. K., & Van Heuven, J. W. (2000b). Introduction to Physical Transport Phenomena. In *Transport Phenomena* (2nd ed., p. 27). Chichester: John Wiley & Sons, Ltd.
- Brooks, A. (2014). *Ionic Liquids : Synthesis, Characterization and Applications*. Hauppauge, New York: Nova Science Publishers, Inc.
- Cao, L., Zhu, P., Zhao, Y., & Zhao, J. (2018). Using machine learning and quantum chemistry descriptors to predict the toxicity of ionic liquids. *Journal of Hazardous Materials*, 352, 17–26.
- Chen, H., Sun, Z., Song, X., & Yu, J. (2017). Operating Regimes and Hydrodynamics of a Rotating-Disc Contactor. *Chemical Engineering and Technology*, *40*(3), 498–505.
- Crowell, K. E. (1997). Agitated Column. In E. Goldberg (Ed.), *Handbook of Downstream Processing* (1st ed., pp. 56, 64–65). New York: Blackie Academic & Professional.
- Cuttica, C. (2018). Background. In *Biodesulfurization in Petroleum Refining* (pp. 1–38). John Wiley & Sons, Incorporated.
- Dataphysics Instruments GmbH. (n.d.). *Interfacial Chemistry: Introduction into Methods of Measuring and Analyzing Contact Angles for the Determination of Surface Free Energies of Solids*. Filderstadt.
- De Haan, A. B., & Bosch, H. (2013). Industrial liquid-liquid extractors. In *Industrial Separation Processes: Fundamentals* (1st ed., p. 131). Berlin/Boston: Walter de Gruyter GmbH.
- Dieselnet. (n.d.). Fuels: European Union. Retrieved April 7, 2020, from https://dieselnet.com/standards/eu/fuel.php
- Dinh, M., Hakimabadi, S. G., & Pham, A. L. T. (2020). Treatment of sulfolane in groundwater: A critical review. *Journal of Environmental Management*, *263*, 110385.
- Domańska, U., Lukoshko, E. V., & Królikowski, M. (2013). Separation of thiophene from heptane with ionic liquids. *Journal of Chemical Thermodynamics*, *61*, 126–131.

- Domańska, U., & Walczak, K. (2015). Ternary liquid-liquid equilibria for mixtures of {Ionic Liquid + Thiophene or Benzothiophene + Heptane} at T = 308.15 K. *Journal of Solution Chemistry*, 44(3–4), 382–394.
- Durski, M., Naidoo, P., Ramjugernath, D., & Domańska, U. (2019). Ternary liquid-liquid phase equilibria of {ionic liquid + thiophene + (octane/hexadecane)}. *Journal of Chemical Thermodynamics*, *134*, 157–163.
- Durski, M., Naidoo, P., Ramjugernath, D., & Domańska, U. (2020). Separation of thiophene from octane/hexadecane with ionic liquids in ternary liquid-liquid phase equilibrium. *Fluid Phase Equilibria*, *509*, 112467.
- European Chemicals Agency. (n.d.-a). Tetrahydrothiophene 1,1-dioxide Registration Dossier. Retrieved June 22, 2020, from https://echa.europa.eu/registration-dossier/-/registereddossier/13657/6/2/6
- European Chemicals Agency. (n.d.-b). Thiophene Registration Dossier. Retrieved June 22, 2020, from https://echa.europa.eu/registration-dossier/-/registered-dossier/12099/6/2/4
- Fahim, M. A., Alsahhaf, T. A., & Elkilani, A. (2010). Hydroconversion. In *Fundamentals of Petroleum Refining* (pp. 153–198).
- Fatemi, M. H., & Izadiyan, P. (2011). Cytotoxicity estimation of ionic liquids based on their effective structural features. *Chemosphere*, *84*(5), 553–563.
- Ficke, L. E., Novak, R. R., & Brennecke, J. F. (2010). Thermodynamic and thermophysical properties of ionic liquid + water systems. *Journal of Chemical and Engineering Data*, 55(11), 4946–4950.
- Frank, T. C., Dahuron, L., Holden, B. S., Prince, W. D., Seibert, A. F., & Wilson, L. C. (2008). Liquid-Liquid Extraction and other Liquid-Liquid Operations and Equipment. In D. W. Green & R. H. Perry (Eds.), *Perry's Chemical Engineers' Handbook* (8th ed., pp. 41, 58–59, 63, 80, 82–85). McGraw Hill Higher Education.
- Freire, M. G., Teles, A. R. R., Rocha, M. A. A., Schröder, B., Neves, C. M. S. S., Carvalho, P. J., ... Coutinho, J. A. P. (2011). Thermophysical characterization of ionic liquids able to dissolve biomass. *Journal* of Chemical and Engineering Data, 56(12), 4813–4822.
- Ge, R., Hardacre, C., Jacquemin, J., Nancarrow, P., & Rooney, D. W. (2008). Heat capacities of ionic liquids as a function of temperature at 0.1 MPa. Measurement and prediction. *Journal of Chemical and Engineering Data*, 53(9), 2148–2153.
- Gharagheizi, F., Ilani-Kashkouli, P., & Mohammadi, A. H. (2012). Group contribution model for estimation of surface tension of ionic liquids. *Chemical Engineering Science*, *78*, 204–208.
- Gómez, E., Domínguez, I., Calvar, N., Palomar, J., & Domínguez, Á. (2014). Experimental data, correlation and prediction of the extraction of benzene from cyclic hydrocarbons using [Epy][ESO4] ionic liquid. *Fluid Phase Equilibria*, *361*, 83–92.
- Gruber, D., Langenheim, D., Gmehling, J., & Moollan, W. (1997). Measurement of activity coefficients at infinite dilution using gas-liquid chromatography. 6. Results for systems exhibiting gas-liquid interface adsorption with 1-octanol. *Journal of Chemical and Engineering Data*, 42(5), 882–885.
- Hansmeier, A. R., Meindersma, G. W., & de Haan, A. B. (2011). Desulfurization and denitrogenation of gasoline and diesel fuels by means of ionic liquids. *Green Chemistry*, *13*(7), 1907–1913.
- Hurley, F. H., & Wier, T. P. (1951). Electrodeposition of Metals from Fused Quaternary Ammonium Salts. *Journal of The Electrochemical Society*, *98*(5), 203.

- Ilbeigi, M., Naziri, F., Fazlali, Al., Foad Aghamiri, S., Talaee, M. R., & Mohammadi, A. H. (2014). Phase behaviour modeling in armoatics extraction from gasoline by ionic liquids. In *Ionic liquids: Sythesis, Characterization and Applications* (pp. 263–280). Nova Science Publishers, Inc.
- IoLiTec. (n.d.-a). 1-Ethyl-3-methylimidazolium methanesulfonate, 99%. Retrieved October 10, 2019, from https://iolitec.de/index.php/products/ionic_liquids/catalogue/imidazolium-based/il-0004-hp
- IoLiTec. (n.d.-b). 1-Ethylimidazolium nitrate, 98%. Retrieved January 21, 2020, from https://iolitec.de/products/ionic_liquids/catalogue/imidazolium-based/il-0272-sg
- Kilbane, J. J., & Le Borgne, S. (2004). Petroleum biorefining: The selective removal of sulfur, nitrogen, and metals. *Studies in Surface Science and Catalysis*, Vol. 151, pp. 29–65.
- Kister, H. Z., Mathias, P. M., Steinmeyer, D. E., Penny, W. R., Crocker, B. B., & Fair, J. R. (2008). Equipment for Distillation, Gas Absorption, Phase Dispersion, and Phase Separation. In D. W. Green & R. H. Perry (Eds.), *Perry's Chemical Engineers' Handbook* (8th ed., p. 40). McGraw Hill Higher Education.
- Kochmodular. (n.d.). Liquid-Liquid Extraction Column Types Agitated and Static. Retrieved April 7, 2020, from https://kochmodular.com/liquid-liquid-extraction/extraction-column-types/
- Kooijman, H. a, & Taylor, R. (2000). The ChemSep Book Second Edition. In *Chempsep Consortium* (p. 468).
- Kowsari, E. (2016). *Ionic Liquids for Green Energy Applications*. Hauppauge, New York: Nova Science Publishers, Inc.
- Królikowski, M. (2019). Liquid–liquid extraction of sulfur compounds from heptane with tricyanomethanide based ionic liquids. *Journal of Chemical Thermodynamics*, *131*, 460–470.
- Kroon, M. C., & Peters, C. J. (2010). Phase Behaviour of Ionic Liquid Systems. In *Applied Thermodynamics of Fluids* (1st ed., pp. 368–393). Royal Society of Chemistry.
- Kumar, A., & Hartland, S. (1987). Prediction of dispersed phase hold-up in rotating disc extractors. *Chemical Engineering Communcations*, *56*, 87–106.
- Kumar, A., & Hartland, S. (1989). Independent prediction of slip velocity and hold-up in liquid/liquid extraction columns. *The Canadian Journal of Chemical Engineering*, *67*(1), 17–25.
- Kumar, A., & Hartland, S. (1992). Prediction of axial mixing coefficients in rotating disc and asymmetric rotating disc extraction columns. *The Canadian Journal of Chemical Engineering*, *70*(1), 77–87.
- Kumar, A., & Hartland, S. (1996). Unified Correlations for the Prediction of Drop Size in Liquid–Liquid Extraction Columns. *Industrial & Engineering Chemistry Research*, *35*(8), 2682–2695.
- Kumar, S., Srivastava, V. C., Nanoti, S. M., & Kumar, A. (2015). Solvent evaluation for desulfurization and denitrification of gas oil using performance and industrial usability indices. *AIChE Journal*, 61(7), 2257–2267.
- Kung, E. Y., & Beckmann, R. B. (1961). Dispersed-phase holdup in a rotating disk extraction column. *AIChE Journal*, 7(2), 319–324.
- Larriba, M., de Riva, J., Navarro, P., Moreno, D., Delgado-Mellado, N., García, J., ... Palomar, J. (2018). COSMO-based/Aspen Plus process simulation of the aromatic extraction from pyrolysis gasoline using the {[4empy][NTf2] + [emim][DCA]} ionic liquid mixture. Separation and Purification Technology, 190, 211–227.
- Larriba, M., Navarro, P., García, J., & Rodríguez, F. (2014). Selective extraction of toluene from n-

heptane using [emim][SCN] and [bmim][SCN] ionic liquids as solvents. *Journal of Chemical Thermodynamics*, 79, 266–271.

- Lazzús, J. A., Cuturrufo, F., Pulgar-Villarroel, G., Salfate, I., & Vega, P. (2017). Estimating the Temperature-Dependent Surface Tension of Ionic Liquids Using a Neural Network-Based Group Contribution Method. *Industrial and Engineering Chemistry Research*, *56*(23), 6869–6886.
- Lazzús, J. A., & Pulgar-Villarroel, G. (2015). A group contribution method to estimate the viscosity of ionic liquids at different temperatures. *Journal of Molecular Liquids, 209,* 161–168.
- Lee, S. H., & Binkley, M. J. (2011). Optimize Design for Distillation Feed. Retrieved May 6, 2020, from Sulzer GTC Technology US Inc. website: https://www.gtctech.com/optimize-design-fordistillation-feed/
- Leng, D. E., & Calabreses, R. V. (2004). Immiscible Liquid-Liquid System. In S. M. Kresta, V. Atiemo-Obeng, & E. L. Paul (Eds.), *Handbook of industrial mixing : science and practice* (1st ed., pp. 639– 754). John Wiley & Sons, Incorporated.
- Liu, X., Chen, Y., Zeng, S., Zhang, X., Zhang, S., Liang, X., ... Kontogeorgis, G. M. (2020). Structure optimization of tailored ionic liquids and process simulation for shale gas separation. AIChE Journal, 66(2), 1–14.
- Ludwig, E. E. (1997). Distillation. In *Applied Process Design for Chemical and Petrochmical Plats, Volume* 2 (3rd ed., p. 134).
- Luis, P., Ortiz, I., Aldaco, R., & Irabien, A. (2007). A novel group contribution method in the development of a QSAR for predicting the toxicity (Vibrio fischeri EC50) of ionic liquids. *Ecotoxicology and Environmental Safety*, *67*(3), 423–429.
- Luyben, W. L. (2013a). Analysis of Distillation Columns. In *Distillation Design and Control Using Aspen Simulation* (2nd ed., pp. 61–77). American Institute of Chemical Engineers.
- Luyben, W. L. (2013b). Setting Up a Steady-State Simulation. In *Distillation Design and Control Using Aspen Simulation* (2nd ed., pp. 78–142). American Institute of Chemical Engineers.
- Mafi, M., Dehghani, M. R., & Mokhtarani, B. (2016). Novel liquid-liquid equilibrium data for six ternary systems containing IL, hydrocarbon and thiophene at 25 °C. *Fluid Phase Equilibria*, 412, 21–28.
- Mafi, M., Dehghani, M. R., & Mokhtarani, B. (2018). Liquid-liquid equilibrium data for extractive desulfurization using 1-butyl-3-methyl imidazolium thiocyanate, n-alkane and thiophene. *Fluid Phase Equilibria*, 456, 109–115.
- Marcilla, A., Reyes-Labarta, J. A., & Olaya, M. M. (2017). Should we trust all the published LLE correlation parameters in phase equilibria? Necessity of their assessment prior to publication. *Fluid Phase Equilibria*, 433, 243–252.
- Marciniak, A., & Królikowski, M. (2012). Ternary (liquid+liquid) equilibria of {trifluorotris(perfluoroethyl)phosphate based ionic liquids+thiophene+heptane}. *The Journal of Chemical Thermodynamics*, 49, 154–158.
- Marciniak, A., & Wlazło, M. (2015). Ternary (liquid + liquid) equilibria of {trifluorotris(perfluoroethyl)phosphate based ionic liquids + thiophene + heptane}: Part 2. *Journal of Chemical Thermodynamics*, *86*, 196–201.
- Morís, M. A., Díez, F. V., & Coca, J. (1997). Hydrodynamics of a rotating disc contactor. *Separation and Purification Technology*, *11*(2), 79–92.
- Murakami, A., Misonou, A., & Inoue, K. (1976). Dispersed phase holdup in a rotating disc extraction

column. Kagaku Kogaku Ronbunshu, 2(3), 256–261.

- Nevers, N. de. (2012). Liquid–liquid, liquid–solid, and gas–solid equilibrium. In *Physical and Chemical Equilibrium for Chemical Engineers* (2nd ed., pp. 181–216). John Wiley & Sons, Incorporated.
- Onink, F., Drumm, C., Meindersma, G. W., Bart, H.-J., & de Haan, A. B. (2010). Hydrodynamic behavior analysis of a rotating disc contactor for aromatics extraction with 4-methyl-butyl-pyridinium·BF4 by CFD. *Chemical Engineering Journal*, *160*(2), 511–521.
- Onink, S. A. F. (2011). *Ionic Liquid Performance in Pilot Plant Contactors for Aromatics Extraction* (Eindhoven University of Technology). Eindhoven University of Technology.
- Oster, K., Jacquemin, J., Hardacre, C., Ribeiro, A. P. C., & Elsinawi, A. (2018). Further development of the predictive models for physical properties of pure ionic liquids: Thermal conductivity and heat capacity. *Journal of Chemical Thermodynamics*, *118*, 1–15.
- Othmer, D., & Tobias, P. (1942). Liquid-Liquid Extraction Data The Line Correlation. *Industrial & Engineering Chemistry*, *34*(6), 693–696.
- Peng, D., & Picchioni, F. (2020). Prediction of toxicity of Ionic Liquids based on GC-COSMO method. *Journal of Hazardous Materials*, 122964.
- Peng, D., Zhang, J., Cheng, H., Chen, L., & Qi, Z. (2017). Computer-aided ionic liquid design for separation processes based on group contribution method and COSMO-SAC model. *Chemical Engineering Science*, 159, 58–68.
- Ramalingam, A., & Balaji, A. (2015). Liquid-liquid equilibrium (LLE) data for ternary mixtures of {[EMIM][EtSO4] + thiophenebenzothiophene + n-hexadecane}and {[EMIM][MeSO3] + thiophene/benzothiophene + n-hexadecane} at 298.15 K. *Journal of Molecular Liquids*, 212, 372–381.
- Ramalingam, A., & Banerjee, T. (2011). COSMO-RS based predictions for the desulphurization of diesel oil using ionic liquids: Effect of cation and anion combination. *Fuel Processing Technology*, 92(1), 39–52.
- Revelli, A. L., Mutelet, F., & Jaubert, J. N. (2010). Extraction of benzene or thiophene from n -Heptane using ionic liquids. NMR and thermodynamic study. *Journal of Physical Chemistry B*, 114(13), 4600–4608.
- Robbins, L. A., & Cusack, R. W. (1997). Liquid-Liquid Extraction Operations and Equipment. In R. H. Perry, D. W. Green, & J. O. Maloney (Eds.), *Perry's Engineers' Handbook* (7th ed., pp. 38–39). McGraw Hill Higher Education.
- Rychlewska, K., Konieczny, K., & Bodzek, M. (2015). Pervaporative desulfurization of gasoline separation of thiophene/n-heptane mixture. *Archives of Environmental Protection*, 41(2), 3–11.
- Salleh, M. Z. M., Hadj-Kali, M. K., Hashim, M. A., & Mulyono, S. (2018). Ionic liquids for the separation of benzene and cyclohexane – COSMO-RS screening and experimental validation. *Journal of Molecular Liquids*, 266, 51–61.
- Salleh, Z., Wazeer, I., Mulyono, S., El-blidi, L., Hashim, M. A., & Hadj-Kali, M. K. (2017). Efficient removal of benzene from cyclohexane-benzene mixtures using deep eutectic solvents COSMO-RS screening and experimental validation. *Journal of Chemical Thermodynamics*, *104*, 33–44.
- Sattari, M., Gharagheizi, F., Ilani-Kashkouli, P., Mohammadi, A. H., & Ramjugernath, D. (2014). Development of a group contribution method for the estimation of heat capacities of ionic liquids. *Journal of Thermal Analysis and Calorimetry*, *115*(2), 1863–1882.

- Sharker, S., Phillips, C. R., & Mumford, C. J. (1985). Characterization of hydrodynamic parameters in rotating disc and oldshue-rushton columns. Hydrodynamic modelling, drop size, hold-up and flooding. *The Canadian Journal of Chemical Engineering*, *63*(5), 701–709.
- Shell Nederland. (n.d.). Over Shell Pernis. Retrieved February 11, 2020, from https://www.shell.nl/over-ons/shell-pernis-refinery/shell-pernis.html
- Singh, D., Chopra, A., Mahendra, P. K., Kagdiyal, V., & Saxena, D. (2016). Sulfur compounds in the fuel range fractions from different crude oils. *Petroleum Science and Technology*, *34*(14), 1248–1254.
- Singh, M. P., Mandal, S. K., Verma, Y. L., Gupta, A. K., Singh, R. K., & Chandra, S. (2014). Viscoelastic, surface, and volumetric properties of ionic liquids [BMIM][OcSO4], [BMIM][PF6], and [EMIM][MeSO3]. Journal of Chemical and Engineering Data, 59(8), 2349–2359.
- Sinnott, R., & Towler, G. (2013a). Capital Cost Estimating. In *Chemical Engineering Design: Principles, Practice and Economics of Plant and Process design* (2nd ed., p. 329). Oxford: Elsevier Ltd.
- Sinnott, R., & Towler, G. (2013b). Heat-Transfer Equipment. In *Chemical Engineering Design: Principles, Practice and Economics of Plant and Process design* (2nd ed., pp. 1047–1106). Oxford: Elsevier Ltd.
- Sinnott, R., & Towler, G. (2013c). Instrumentation and Process Control. In *Chemical Engineering Design: Principles, Practice and Economics of Plant and Process design* (2nd ed., pp. 251–275). Oxford: Elsevier Ltd.
- Sinnott, R., & Towler, G. (2013d). Materials of Construction. In *Chemical Engineering Design: Principles, Practice and Economics of Plant and Process design* (2nd ed., pp. 279–306). OXford: Elsevier Ltd.
- Sinnott, R., & Towler, G. (2013e). Separation Columns (Distillation, Absorption, and Extraction). In *Chemical Engineering Design: Principles, Practice and Economics of Plant and Process design* (2nd ed., pp. 807–935). Oxford: Elsevier Ltd.
- Sinnott, R., & Towler, G. (2013f). Separation Columns (Distrillation, Absorption, and extraction). In *Chemical Engineering Design: Principles, Practice and Economics of Plant and Process design* (2nd ed., p. 917). Oxford: Elsevier Ltd.
- Sinnott, R., & Towler, G. (2013g). Utilities and Energy Efficient Design. In *Chemical Engineering Design: Principles, Practice and Economics of Plant and Process design* (2nd ed., pp. 104–113). Oxford: Elsevier Ltd.
- Skelland, A. H. P., & Seksaria, R. (1978). Minimum Impeller Speeds for Liquid-Liquid Dispersion in Baffled Vessels. Industrial & Engineering Chemistry Process Design and Development, 17(1), 56– 61.
- Smith, C. L. (2012). Reboilers and Feed Preheaters. In *Distillation Control* (1st ed., pp. 180–208). John Wiley & Sons, Incorporated.
- Smith, J. ., Van Ness, H. C., & Abbott, M. M. (2005a). Solution thermodynamics: theory. In *Introduction to chemical engineering thermodynamics* (7th ed., pp. 378–429). McGraw Hill Higher Education.
- Smith, J. ., Van Ness, H. C., & Abbott, M. M. (2005b). Topics in phase equilibria. In *Introduction to chemical engineering thermodynamics* (7th ed., pp. 583–589). McGraw Hill Higher Education.
- Song, Z., Zhang, C., Qi, Z., Zhou, T., & Sundmacher, K. (2018). Computer-aided design of ionic liquids as solvents for extractive desulfurization. *AIChE Journal*, *64*(3), 1013–1025.
- TLV. (2020). Calculator: Superheated Steam Table. Retrieved May 30, 2020, from https://www.tlv.com/global/ME/calculator/superheated-steam-table.html

- Valderrama, J. O., & Rojas, R. E. (2009). Critical properties of ionic liquids. Revisited. *Industrial and Engineering Chemistry Research*, *48*(14), 6890–6900.
- Valderrama, J. O., Sanga, W. W., & Lazzús, J. A. (2008). Critical properties, normal boiling temperature, and acentric factor of another 200 ionic liquids. *Industrial and Engineering Chemistry Research*, 47(4), 1318–1330.
- Van der Akker, H., & Mudde, R. F. (2014). Fluid mechanics. In *Transport Phenomena: the Art of Balancing* (1st ed., p. 276). Delft Academic Press.
- Visscher, F. (2013). *Liquid-liquid processes in spinning disc equipment door* (Eindhoven University of Technology). Eindhoven University of Technology.
- Welton, T. (2018). Ionic liquids: a brief history. Biophysical Reviews, 10(3), 691–706.
- Westerterp, K. R., & Landsman, P. (1962). Axial mixing in a rotating disk contactor-I Apparent longitudinal diffusion. *Chemical Engineering Science*, 17(5), 363–372.
- Wu, K.-J., Zhao, C. X., & He, C. H. (2013). Development of a group contribution method for determination of thermal conductivity of ionic liquids. *Fluid Phase Equilibria*, *339*, 10–14.
- Zhang, X. J., Wang, J. Y., & Hu, Y. Q. (2010). Interfacial tension of n -alkane and ionic liquid systems. *Journal of Chemical and Engineering Data*, 55(11), 4687–4690.

Appendix

A Matlab screening

Matlab code used for allowing wider temperature range in Matlab screening:

```
L=length(num(:,2));
for P=1:L
    if num(P,2)>=(T+1)|num(P,2)<=(T-1);
    index3(P,1)=0;
    else
    index3(P,1)=1;
    end
end</pre>
```

Table 12 selected ionic liquids for thiophene/n-heptane (black is no LLE available and available for purchase, green LLE available)

Cation	Anion	Name of ionic liquid		β	S	T(K)
EMIM	MeSO ₃	1-ethyl-3-methylimidazolium methanesulfonate		0.5	739.8	323
EMIM	NO ₃	1-ethyl-3-methylimidazolium nitrate		0.7	333.8	318
PYR-4,1	DCA	1-butyl-1-methylpyrrolidinium dicyanamide	104.9	1.2	89.3	318
BMIM	SCN	1-butyl-3-methylimidazolium thiocyanate	190.7	0.8	231.5	298
DMIM	MP	1,3-dimethylimidazolium methylphosphonate	737.6	0.4	1756.2	298

Table 13 selected ionic liquids for thiophene/n-octane (black is no LLE available and available for purchase, green LLE available, red purchase not possible)

Cation	Anion	Name of ionic liquid	PI	β	S	Т(К)
Pyr-	SCN	1-(3-cyanopropyl)-1-methyl pyrrolidinium	331.1	0.4	824.5	318
3CN,C1		thiocyanate				
PYR-4,1	SCN	1-butyl-1-methylpyrrolidinium	275.8	1.0	273.9	298
		thiocyanate				
BMIM	SCN	1-butyl-1-methylpyrrolidinium	237.5	0.8	288.3	298
		thiocyanate				
MO-2,1	DCA	N-ethyl-N-methylmorpholium	226.0	0.4	506.3	318
		dicyanamide				
EMIM	MeSO₃	1-ethyl-3-methylimidazolium	206.3	0.5	394.0	323
		methanesulfonate				
EMIM	MeSO₃	1-ethyl-3-methylimidazolium	177.3	0.5	365.3	323
		methanesulfonate				
EMIM	NO ₃	1-ethyl-3-methylimidazolium nitrate	331.8	0.7	461.2	318

B Experimental and Results

B1 Internal standard GC

Table 14 Internal standard line creation for n-octane systems, mass fraction nonane in n-Nonane/n-octane stock solution=1.004% and mass fraction Thiophene in Thiophene/n-heptane stock solution=9.631%. Obtained RRF=0.6676.

vial number	M(thio,C7 stock) g	M(C9,C7 stock) g	A(Thio)	A(c9)
1	0.2672	4.7608	316.4	929.4
2	0.4973	4.5001	605.4	875.2
3	1.0081	4.2057	1202.8	785.5
4	1.0282	2.0053	2112.5	644.9
5	1.5707	1.5599	3109	483.2

Table 15 Internal standard line creation for n-heptane systems, mass fraction nonane in n-Nonane/n-heptane stock solution=1.000% and mass fraction Thiophene in Thiophene/n-heptane stock solution=10.01%. Obtained RRF=0.6581.

vial number	M(thio,C7 stock) g	M(C9,C7 stock) g	Athio+imp	A(Thio)	A(c9)
1	0.266	4.859	743.000	366.905	948.800
2	0.514	4.530	1080.300	704.205	930.700
3	1.014	4.032	1764.700	1388.605	820.200
4	1.002	1.997	2651.800	2275.705	686.200
5	1.515	1.522	3759.400	3383.305	514.600



Figure 40 RRF for the n-heptane system



Figure 41 RRF for the n-octane system
B2 GC results

Table 16 GC results for the [EMIM][MeSO₃]/Thiophene/n-octane systems

wt% thiophene	mass top layer g	mass c8/c9 stock g	A thiophene	A nonane
5	0.0513	1.1873	186.4	1090.4
10	0.0517	1.1306	425.3	1091.9
15	0.0421	1.1547	530.6	1103.4
20	0.0284	1.2157	460.7	1118.8
25	0.0411	1.0887	980.1	1083.1
30	0.0522	1.1015	1571.4	1090

Table 17 GC results for the [EMIM][MeSO₃]/Thiophene/n-heptane systems

wt% thiophene	mass top layer g	mass c7/c9 stock g	A thio+imp	Athio	A nonane
5	0.0419	1.1452	570.5	150.2	1020.9
10	0.0534	1.1649	821.9	401.6	1005.3
15	0.0178	1.0645	657.3	237.989	1053.8
20	0.0524	1.0898	1377.4	958.089	1053.7
25	0.0235	1.0841	985.9	566.589	1079.5
30	0.0494	1.0569	1932.3	1512.989	1055.8

Table 18 GC results for the [EIM][NO₃]/Thiophene/n-octane systems

wt% thiophene	mass top layer g	mass c8/c9 stock g	A thiophene	A nonane
5	0.026	1.0394	108.80	1047.3
10	0.0305	1.0695	247.20	1046.3
15	0.0464	1.0514	620.10	1022.1
20	0.0313	1.141	543.00	1041.3
25	0.052	1.1104	1219.80	1021.4
30	0.0629	1.1461	1762.50	1013.1

Table 19 GC results for the [EIM][NO₃]/Thiophene/n-heptane systems

wt% thiophene	mass top layer g	mass c7/c9 stock g	A thio+imp	Athio	A nonane
5	0.036	1.0991	566.10	145.80	1024.7
10	0.0375	1.0547	759.60	340.29	1031.7
15	0.0281	1.0889	807.70	388.39	1070.8
20	0.0511	1.0208	1470.40	1051.09	1049.2
25	0.0422	1.1427	1433.80	1013.50	1005.8
30	0.057	1.1025	2144.70	1724.40	1055.3

B3 H-NMR results

Table 20 H-NRM results for the [EMIM][MeSO₃]/Thiophene/n-octane systems

wt% thiophene	Athio	AIL	Ac8
5	0.0574	1	0.02595
10	0.11387	1	0.00369
15	0.18383	1	0.00667
20	0.24744	1	0.0079
25	0.31026	1	0.00394
30	0.39148	1	0.00521

Table 21 H-NRM results for the [EMIM][MeSO₃]/Thiophene/n-heptane systems

wt% thiophene	Athio	AIL	Ac7
5	0.05761	1	0.00616
10	0.12687	1	0.00539
15	0.17571	1	0.00528
20	0.23658	1	0.00441
25	0.29917	1	0.01147
30	0.38975	1	0.00472

Table 22 H-NMR results for the [EIM][NO₃]/Thiophene/n-octane systems

wt% thiophene	Athio	AIL	Ac8
5	0.07154	1	0.01221
10	0.12897	1	0.01142
15	0.21988	1	0.0108
20	0.25783	1	0.00883
25	0.33737	1	0.01013
30	0.43315	1	0.01247

Table 23 H-NMR results for the [EIM][NO₃]/Thiophene/n-heptane systems

wt% thiophene	Athio	AIL	Ac7
5	0.05864	1	0.00862
10	0.10151	1	0.0155
15	0.1933	1	0.01136
20	0.24047	1	0.01504
25	0.32339	1	0.00979
30	0.40694	1	0.01286

B4 Known LLE data sources

Table 24 sources for different ionic liquid data for thiophene/n-heptane extraction depicted in Figure 9 and Figure 10

Ionic liquid and temperature I	Source
[BMPYR][FAP] 25C	(Domańska et al., 2013)
[BMPYR][TCB] 25C	(Domańska et al., 2013)
[BMPYR][TC] 25C	(Domańska et al., 2013)
[PMPIP][NTf2] 35C	(Domańska & Walczak, 2015)
[P-2,4,4,4][DEP] 35C	(Domańska & Walczak, 2015)
[BMIM][BF4] 25C	(Revelli, Mutelet, & Jaubert, 2010)
[DMIM][MP] 25C	(Revelli et al., 2010)
[BMIM][SCN] 25C	(Revelli et al., 2010)
[COC ₂ mMOR][FAP] 25C	(Marciniak & Królikowski, 2012)
[COC ₂ mPIP][FAP] 25C	(Marciniak & Królikowski, 2012)
[COC ₂ mPYR][FAP] 25C	(Marciniak & Królikowski, 2012)
[EMIM][FAP] 25C	(Marciniak & Wlazło, 2015)
[C ₂ Ohmim][FAP] 25C	(Marciniak & Wlazło, 2015)
[COC ₂ N-1,1,2][FAP] 25C	(Marciniak & Wlazło, 2015)
[BMMOR][TCM] 35C	(Królikowski, 2019)
[HMMOR][TCM] 35C	(Królikowski, 2019)

Table 25 sources for different ionic liquid data for thiophene/n-octane extraction depicted in Figure 11 and Figure 12

Ionic liquid and temperature I	Source
[BMIM][SCN] 25C	(Mafi et al., 2018)
[OMIM][SCN] 25C	(Mafi, Dehghani, & Mokhtarani, 2016)
[HMIM][SCN] 25C	(Mafi et al., 2016)
[OHOHIM][NTf ₂] 35C	(Durski, Naidoo, Ramjugernath, & Domańska, 2019)
[BMIM][Otf] 35C	(Durski et al., 2019)
[BMPIP][DCA] 35C	(Durski, Naidoo, Ramjugernath, & Domańska, 2020)
[Pi4,i4,i4,1][TOS] 35C	(Durski et al., 2020)

B5 Tie lines

Table 26 Experimental results for the [EMIM][MeSO₃]/Thiophene/n-octane systems

mass% thiophene	x1HC	x2HC	x3HC	x1IL	x2IL	x3IL	S	β	mass balance %
0.05	0.00	0.08	0.92	0.90	0.09	6.7E-03	151.9	1.11	1.46%
0.10	0.00	0.17	0.83	0.85	0.15	1.6E-03	464.3	0.88	7.59%
0.15	0.00	0.25	0.75	0.78	0.22	2.6E-03	246.3	0.86	5.08%
0.20	0.00	0.33	0.67	0.73	0.27	2.9E-03	192.0	0.82	8.32%
0.25	0.00	0.43	0.57	0.68	0.32	1.3E-03	308.9	0.73	5.94%
0.30	0.00	0.53	0.47	0.63	0.37	1.6E-03	197.0	0.69	4.50%

Table 27 Experimental results for the [EMIM][MeSO₃]/Thiophene/n-heptane systems

mass% thiophene	x1HC	x2HC	хЗНС	x1IL	x2IL	x3IL	S	β	mass balance %
0.05	0.00	0.06	0.94	0.92	0.08	2.8E-03	420.9	1.27	5.59%
0.10	0.00	0.14	0.86	0.84	0.16	2.3E-03	451.6	1.18	-0.21%
0.15	0.00	0.21	0.79	0.79	0.21	2.1E-03	377.4	1.00	4.07%
0.20	0.00	0.29	0.71	0.74	0.26	1.6E-03	389.6	0.89	3.77%
0.25	0.00	0.37	0.63	0.69	0.31	3.9E-03	131.2	0.83	5.67%
0.30	0.00	0.47	0.53	0.63	0.37	1.5E-03	277.2	0.78	2.46%

mass% thiophene	x1HC	x2HC	хЗНС	x1IL	x2IL	x3IL	S	β	mass balance %
0.05	0.00	0.08	0.92	0.93	0.07	3.8E-03	194.43	0.80	2.57%
0.10	0.00	0.16	0.84	0.88	0.11	3.4E-03	175.42	0.70	8.32%
0.15	0.00	0.26	0.74	0.82	0.18	2.9E-03	172.70	0.69	-0.14%
0.20	0.00	0.35	0.65	0.79	0.20	2.3E-03	161.26	0.58	6.34%
0.25	0.00	0.46	0.54	0.75	0.25	2.5E-03	118.37	0.55	3.28%
0.30	0.00	0.55	0.45	0.70	0.30	2.9E-03	84.31	0.55	1.21%

Table 28 Experimental results for the [EIM][NO₃]/Thiophene/n-octane systems

Table 29 Experimental results for the [EIM][NO₃]/Thiophene/n-heptane systems

mass% thiophene	x1HC	x2HC	x3HC	x1IL	x2IL	x3IL	S	β	mass balance %
0.05	0.00	0.07	0.93	0.94	0.06	2.7E-03	281.9	0.82	5.47%
0.10	0.00	0.14	0.86	0.90	0.09	4.7E-03	116.9	0.64	7.74%
0.15	0.00	0.22	0.78	0.84	0.16	3.2E-03	183.5	0.74	3.20%
0.20	0.00	0.31	0.69	0.80	0.19	4.0E-03	107.2	0.62	3.81%
0.25	0.00	0.42	0.58	0.75	0.24	2.5E-03	136.6	0.58	-4.41%
0.30	0.00	0.49	0.51	0.71	0.29	3.0E-03	100.3	0.59	-0.95%

C NRTL results

Table 30 NRTL results for the [EMIM][MeSO₃]/Thiophene/n-octane systems

Experimental						NRTL					
	IL layer			HC layer	IL layer			HC layer			
IL	thiophene	HC	IL	thiophene	HC	IL	thiophene	HC	IL	thiophene	HC
0.904	0.090	0.007	0	0.081	0.919	0.915	0.083	0.002	0.002	0.087	0.911
0.853	0.146	0.002	0	0.166	0.834	0.837	0.158	0.004	0.002	0.176	0.822
0.782	0.216	0.003	0	0.251	0.749	0.771	0.222	0.007	0.002	0.263	0.735
0.727	0.270	0.003	0	0.329	0.671	0.712	0.278	0.01	0.002	0.356	0.642
0.682	0.317	0.001	0	0.433	0.567	0.664	0.324	0.012	0.001	0.455	0.544
0.629	0.369	0.002	0	0.534	0.466	0.625	0.361	0.014	0.001	0.562	0.437

Table 31 NRTL results for the [EMIM][MeSO₃]/Thiophene/n-heptane systems

Experimental						NRTL					
	IL layer			HC layer		IL layer			HC layer		
IL	thiophene	HC	IL	thiophene	HC	IL	thiophene	HC	IL	thiophene	HC
0.918	0.079	0.003	0	0.063	0.938	0.921	0.076	0.003	0.002	0.070	0.929
0.838	0.160	0.002	0	0.135	0.865	0.849	0.145	0.005	0.001	0.143	0.856
0.790	0.208	0.002	0	0.209	0.791	0.782	0.209	0.009	0.001	0.220	0.779
0.737	0.262	0.002	0	0.292	0.708	0.721	0.266	0.013	0.001	0.303	0.696
0.688	0.309	0.004	0	0.374	0.626	0.667	0.316	0.017	0.001	0.392	0.607
0.630	0.368	0.002	0	0.472	0.528	0.620	0.361	0.019	0.001	0.491	0.508

Experimental						NRTL					
	IL layer	HC layer			IL layer			HC layer			
IL	thiophene	HC	IL	thiophene	HC	IL	thiophene	HC	IL	thiophene	HC
0.930	0.067	0.004	0	0.083	0.917	0.937	0.061	0.003	0.008	0.090	0.902
0.883	0.114	0.003	0	0.162	0.838	0.879	0.117	0.004	0.007	0.178	0.815
0.817	0.180	0.003	0	0.261	0.739	0.824	0.170	0.006	0.006	0.268	0.726
0.793	0.205	0.002	0	0.352	0.648	0.773	0.219	0.008	0.005	0.364	0.631
0.746	0.252	0.003	0	0.458	0.542	0.730	0.261	0.009	0.004	0.465	0.531
0.696	0.301	0.003	0	0.553	0.447	0.697	0.293	0.010	0.003	0.566	0.432

Table 32 NRTL results for the [EIM][NO₃]/Thiophene/n-octane systems

Table 33 NRTL results for the [EIM][NO₃]/Thiophene/n-heptane systems

Experimental						NRTL						
	IL layer		HC layer				IL layer			HC layer		
IL	thiophene	HC	IL	thiophene	HC	IL	thiophene	HC	IL	thiophene	HC	
0.942	0.055	0.003	0	0.068	0.933	0.947	0.051	0.001	0.001	0.075	0.924	
0.904	0.092	0.005	0	0.144	0.856	0.895	0.102	0.003	0.001	0.152	0.847	
0.835	0.162	0.003	0	0.218	0.782	0.843	0.152	0.006	0.001	0.233	0.767	
0.803	0.193	0.004	0	0.309	0.691	0.792	0.199	0.009	0.001	0.318	0.681	
0.754	0.244	0.003	0	0.421	0.580	0.745	0.242	0.012	0.001	0.407	0.593	
0.709	0.288	0.003	0	0.486	0.514	0.702	0.282	0.015	0.001	0.506	0.493	

D NRTL check-up

Here all the other graphs of the NRTL check-up are presented. The graphs of the $[EIM][NO_3]$ and n-heptane system is shown in the main text.

D1 [EIM][NO₃]/n-Octane









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D3 [EMIM][MeSO₃]/n-Octane





E Properties

Aspen uses the following formulas to calculated properties at different temperatures in K, see Equation 53 to Equation 56. The critical temperature is obtained using the work of (Valderrama & Rojas, 2009), who employ group contribution theory to calculate the critical properties of the ionic liquid. The critical properties of [EMIM][MeSO₃] were already calculated, [EIM][NO₃] was calculated using their excel file. The constants for Equation 53 to Equation 56, for [EMIM][MeSO₃] are shown in Table 34 and are obtained by fitting experimental data of [EMIM][MeSO₃] versus the temperature in excel for Equation 53 and Equation 55. The data fitting for Equation 54 and Equation 56 was done using the built-in function of Matlab. The results of [EIM][NO₃] is shown in Table 35. All fits had R² higher than 0.99. The ideal gas heat capacity was calculated using the critical properties and the liquid heat capacity, using the work of (Ge, Hardacre, Jacquemin, Nancarrow, & Rooney, 2008).

No experimental property data is available for [EIM][NO₃] and therefore a different method needs to be found to calculate the Aspen property formulas.

- The **Density** was calculated using the excel file of (Valderrama & Rojas, 2009), by making a row of different temperatures and fitting the data points, using Equation 53. The average absolute relative deviation (AARD) for the density and critical properties were obtained from a previous work of the author, namely (Valderrama, Sanga, & Lazzús, 2008).
- The **viscosity** was calculated using the work of (Lazzús & Pulgar-Villarroel, 2015), by applying their group contribution method to Matlab and fitting the data points using Equation 54.
- The liquid heat capacity was calculated from the ideal gas heat capacity, using the method proposed by (Ge et al., 2008), similarly to the ideal gas heat capacity of [EMIM][MeSO₃], but now the other way around. The liquid heat capacity was also calculated using (Sattari, Gharagheizi, Ilani-Kashkouli, Mohammadi, & Ramjugernath, 2014), however, these results were inadequate (heat capacity remained constant) and it was decided to use the work of (Ge et al., 2008; Oster, Jacquemin, Hardacre, Ribeiro, & Elsinawi, 2018).
- The **ideal gas heat capacity** of [EIM][NO₃] was calculated using the method proposed by (Ge et al., 2008) and updated by (Oster et al., 2018).
- The surface tension was calculated using the group contribution method from (Gharagheizi, Ilani-Kashkouli, & Mohammadi, 2012). The calculated data was fitted to Equation 56. The surface tension was also calculated using the work of (Lazzús, Cuturrufo, Pulgar-Villarroel, Salfate, & Vega, 2017), however, in this work the surface seems to be increasing with temperature, up to 340K, where it starts decreasing. In Table 35 the statistical parameters for the works referenced are depicted, and because of the better parameters of the work of (Lazzús et al., 2017), it was decided to use their values for the surface tension of [EIM][NO₃]. (Lazzús et al., 2017) uses MAPE (mean absolute percentage error) instead of AARD, they are comparable to each other.
- The **thermal conductivity** had to be calculated using group contribution theory for both ionic liquids, which was done using the method proposed by (Wu, Zhao, & He, 2013) and updated by (Oster et al., 2018).

$$\rho = C_1 + C_2 T$$

Equation 53 Aspen density calculation (kg/m^3) with T in K (Liu et al., 2020)

$$\ln \eta = C_1 + \frac{C_2}{T} + C_3 \ln T$$

Equation 54 Aspen viscosity calculation (Pa.s) with T in K (Liu et al., 2020)

$$C_p = C_1 + C_2 T + C_3 T^2$$

Equation 55 Aspen heat capacity calculation (J/(K.mol)) with T in K (Liu et al., 2020)

$$\sigma = C_1 \left(1 - \frac{T}{T_{cr}} \right)^{C_2 + \frac{C_3 T}{T_{cr}}}$$

Equation 56 Aspen surface tension calculation (N/m) with T in K and T_c the critical temperature of the ionic liquid (Liu et al., 2020)

$$\lambda = C_1 + C_2 T + C_3 T^2$$

Equation 57 Aspen thermal conductivity (W/mK) with T in K (Liu et al., 2020)

Table 34 Properties of [EMIM][MeSO₃], using experimental data

[EMIM][MeSO ₃]				
Property	Value at 298.15K	Reference	Aspen formula	Reference
Molecular weight (g/mol)	206.26	(IoLiTec, n.da)	N.A.	N.A.
Boiling point (K)	667.4	Calculated using (Valderrama & Rojas, 2009) (AARD=5.9%)	N.A.	N.A.
Density (kg/m³)	1242.4	(Freire et al., 2011)	C1=1443.1 C2=-0.6721 R ² =0.9994	(Freire et al., 2011)
Viscosity (Pa s)	0.135	(IoLiTec, n.da)	C1=-349.2 C2=20300 C3=49.03 R ² =0.9996	(Freire et al., 2011)
Liquid heat capacity (J/K*mol)	345.52 (not in line with Ficke et al.)	(Freire et al., 2011)	C1=698.91 C2=-2.7315 C3=0.005 R ² =0.9961	(Ficke, Novak, & Brennecke, 2010)
Ideal gas heat capacity (J/K*mol)	260.0	Calculated using (Ge et al., 2008)	C1=502.84 C2=-2.1827 C3=0.0044 R ² =0.9981	Calculated using (Ge et al., 2008)
Surface tension (N/m)	0.0451	(Anantharaj & Banerjee, 2013)	C1=0.06575 C2=0.5415 C3=1.249 R ² =0.9947	(M. P. Singh et al., 2014)
Thermal conductivity (W/mK)	0.197	Calculated using (Oster et al., 2018)	C1=0.243954 C2=- 1.141574*10 ⁻⁴ C3=- 5.52252*10 ⁻⁸ R ² =1	Calculated using (Oster et al., 2018)
Critical temperature (K)	1026.0	Calculated using (Valderrama & Rojas, 2009) (AARD=5.9%)	N.A.	N.A.

Critical pressure (bar)	48.13	Calculated using (Valderrama & Rojas,	N.A.	N.A.
		2009) (AARD=5.9%)		
Critical volume, V _{cr}	587.1	Calculated using	N.A.	N.A.
(cm³/mol)		(Valderrama & Rojas,		
		2009) (AARD=5.9%)		
Critical	0.3312	Calculated using	N.A.	N.A.
compressibility, Z _{cr}		(Valderrama & Rojas,		
		2009) (AARD=5.9%)		
Acentric factor, ω	0.3307	Calculated using	N.A.	N.A.
		(Valderrama & Rojas,		
		2009) (AARD=5.9%)		

Table 35 Properties of [EIM][NO3] using calculated data

[EIM][NO₃]					
Property	Value at 298.15K	Reference	Aspen formula	Reference	Statistical parameters of reference
Molecular weight (g/mol)	159.14	(loLiTec, n.db)	N.A.	N.A.	N.A.
Boiling point (K)	620.8	Calculated using (Valderrama & Rojas, 2009) (AARD=5.9%)	N.A.	N.A.	
Density (kg/m³)	1250.1	Calculated using (Valderrama & Rojas, 2009)	C1=1274.6 C2=- 0.0821 R ² =1	Calculated using (Valderrama & Rojas, 2009)	AARD=5.9% ¹
Viscosity (Pa s)	0.116	Calculated using (Lazzús & Pulgar- Villarroel, 2015)	C1=-27.49 C2=7551 C3-2.832e- 06 R ² =1.000	Calculated using (Lazzús & Pulgar- Villarroel, 2015)	AARD=4.55% R ² =0.9359 N=1445
Liquid heat capacity (J/K*mol)	418.0	Calculated using (Ge et al., 2008)	C1=392.72 C2=- 0.1832 C3=9*10 ⁻⁴ R ² =1.000	Calculated using (Ge et al., 2008)	AARD=2.9% N=961
Ideal gas heat capacity (J/K*mol)	286.3	Calculated using (Oster et al., 2018)	C1=73.46 C2=0.7625 C3=- 1.948*10 ⁻⁴ R ² =1.000	Calculated using (Oster et al., 2018)	AARD=4.28% N=3646
Surface tension (N/m)	0.0717	Calculated using (Lazzús et al., 2017)	C1=0.1131 C2=1.249 C3=-0.431 R ² =1.000	Calculated using (Lazzús et al., 2017)	MAPE=1.18% R=0.996 N=2307
Thermal conductivity (W/mK)	0.199	Calculated using (Oster et al., 2018)	C1=0.256 C2=- 0.0002	Calculated using (Oster et al., 2018)	AARD: 1.66% N=399

¹ AARD obtained from previous work (Valderrama et al., 2008)

			C3=- 9.0*10 ⁻⁸ R ² =1		
Critical temperature (K)	880.1	Calculated using (Valderrama & Rojas, 2009)	N.A.	N.A.	AARD=5.9%
Critical pressure (bar)	40.03	Calculated using (Valderrama & Rojas, 2009)	N.A.	N.A.	AARD=5.9%
Critical volume, V _{cr} (cm ³ /mol)	450.3	Calculated using (Valderrama & Rojas, 2009) (AARD=5.9%)	N.A.	N.A.	AARD=5.9%
Critical compressibility, Z _{cr}	0.2464	Calculated using (Valderrama & Rojas, 2009) (AARD=5.9%)	N.A.	N.A.	AARD=5.9%
Acentric factor, ω	0.6393	Calculated using (Valderrama & Rojas, 2009) (AARD=5.9%)	N.A.	N.A.	AARD=5.9%



Figure 42 density of ionic liquids versus temperature



Figure 43 viscosity of ionic liquids versus temperature



Figure 44 liquid heat capacity of ionic liquids versus temperature



Figure 45 ideal gas heat capacity of ionic liquids versus temperature



Figure 46 surface tension of ionic liquids versus temperature



Figure 47 thermal conductivity of ionic liquids versus temperature

E1 Viscosity calculation

The viscosity of an ionic liquid can be determined using a group contribution theory developed by Juan Lazzús and Geraldo Pulgar-Villarroel (Lazzús & Pulgar-Villarroel, 2015). The formula depicted in Equation 58 calculated the viscosity in cP using a few parameters. C is defined as 6.982, n_i and n_j depict the number of occurrences of a certain group, a^+ and b^+ are contributions for the cation, lastly, a^- and b^- are the contributions for the anion. The contributions were obtained by (Lazzús & Pulgar-Villarroel, 2015) by using a database of known ionic liquids. Unfortunately, the viscosity for [EMIM][MeSO₃] could not be calculated, due to the limited amount of available contribution parameters for the anion. IoLiTec, the supplier of the ionic liquid, reported the viscosity to be 135 cP (0.135 Pa.s) (IoLiTec, n.d.-a). Using Equation 58 the viscosity for [EIM][NO₃] was found to be 116 cP at 298 K. IoLiTec has no viscosity provided on their webpage.

$$\operatorname{Ln} \eta = C + \left(\sum_{i} n_{i} a_{i}^{+} + \frac{\sum_{i} n_{i} b_{i}^{+}}{T}\right) + \left(\sum_{j} n_{j} a_{j}^{-} + \frac{\sum_{j} n_{j} b_{j}^{-}}{T}\right)$$

Equation 58 viscosity calculation using group contribution theory (Lazzús & Pulgar-Villarroel, 2015)

The database of contributions was imported into Matlab and by creating an array for the different groups together with their number of occurrences, an easy code can be written to calculate the viscosity.

```
Ni=zeros(1,20);
nj=zeros(1,67);
T=298;
ni([1 11 12 13])=[1 2 1 1];
nj(38)=1;
viscos(ni,nj,T)
function N=viscos(ni,nj,T)
load parameters.mat aplus bplus amin bmin
C=6.982;
N=exp(C+ni*aplus+nj*amin+(ni*bplus+nj*bmin)./T)
End
```

E2 Surface tension

(Lazzús et al., 2017) supplies a Matlab code with their work, which calculated the surface tension of an ionic liquid, using a group contribution method, at a set temperature. This can be done by changing the input vector according to the guide in their article. The obtained results can then be fitted with Equation 56.

E3 heat capacity

The ideal gas heat capacity can be calculated according to Equation 59, which employs group contribution theory, and related to the liquid heat capacity using Equation 60 (Ge et al., 2008; Oster et al., 2018). The values that need to be entered at A, B, C and D in Equation 59 are given in (Oster et al., 2018). In Equation 60 T_r is the reduced temperature and is defined as the temperature divided by the critical temperature, which is given by (Valderrama et al., 2008), and is 1026 K and 880.1 K for [EMIM][MeSO₃] and [EIM][NO₃] respectively. Ω is the acentric factor and is also given by (Valderrama et al., 2008) and is 0.3307 and 0.6393 for [EMIM][MeSO₃] and [EIM][NO₃] respectively.

$$C_p^{ig}(T) = \left[\sum_k n_k A_{Cpk} - 37.93\right] + \left[\sum_k n_k B_{Cpk} + 0.210\right] T + \left[\sum_k n_k C_{Cpk} - 3.91 * 10^{-4}\right] T^2 + \left[\sum_k n_k D_{Cpk} + 2.06 * 10^{-7}\right] T^3$$

Equation 59 ideal gas heat capacity calculation according to (Ge et al., 2008), with constants given by (Oster et al., 2018)

$$\frac{C_p^l - C_p^{lg}}{R} = 1.586 + \frac{0.49}{1 - T_r} + \omega \left(4.2775 + \frac{6.3(1 - T_r)^{1/3}}{T_r} + \frac{0.4355}{1 - T_r} \right), \qquad T_r = \frac{T_r}{T_{cr}}$$

Equation 60 Relation between liquid and ideal gas heat capacity, with the reduced temperature (T/Tcritical) and ω the acentric factor (Ge et al., 2008)

E4 Thermal conductivity

The thermal conductivity can be calculated using a group contribution method proposed by (Wu et al., 2013) and with their group contribution constants expanded by (Oster et al., 2018). The results can then be fitted to Equation 57 to obtain the constants.

$$\lambda = \sum_{i=0}^{2} a_{i} \left(\sum_{j=1}^{k} n_{j} \Delta \lambda_{0,j} \right)^{i} \left[1 + k_{0} \left(1 - \frac{T}{T_{cr}} \right)^{\frac{2}{3}} \right]$$

Equation 61 Thermal conductivity related to temperature according to (Wu et al., 2013), *with group contribution constants given by* (Oster et al., 2018).

E5 Critical properties, acentric factor, and density

The critical properties, e.g. temperature, pressure, volume, compressibility, and the acentric factor are given by (Valderrama et al., 2008), for this they employ a group contribution method. In their work they provide an excel file to calculate missing ionic liquids, which was done for $[EIM][NO_3]$. The excel file also calculated the density and compares this to the density from literature. Because the density of $[EIM][NO_3]$ was missing in literature, the value as calculated by the work of (Valderrama et al., 2008) is used.

F NRTL Aspen Plus





G Process design

G1 Solvent to feed ratio extraction

Table 36 Solvent feed and solvent to feed ratio (S/F) for both ionic liquids, vs. the number of stages

Number stages	[EMIM][MeSO₃] feed	S/F	[EIM][NO₃] feed	S/F
2	106900	10.69	134916	13.4916
3	52900	5.29	67276	6.7276
4	37200	3.72	47465	4.7465
5	30200	3.02	38630	3.863
6	26050	2.605	33736	3.3736
7	23660	2.366	30681	3.0681
8	22065	2.2065	28614	2.8614
9	20925	2.0925	27133	2.7133
10	20070	2.007	26027	2.6027
11	19415	1.9415	25173	2.5173
12	18890	1.889	24497	2.4497
15	17840	1.784	23123	2.3123
20	16900	1.69	21915	2.1915

G2 Dispersed phase calculation

$$\varphi_L = \frac{\phi_{V,L}}{\phi_{V,total}} = \frac{14.453}{26.877} = 0.538$$

$$\chi = \frac{0.538}{1 - 0.538} * \left(\frac{697.9 * 0.135}{1242.4 * 4.41 * 10^{-4}}\right)^{0.3} = 5.45$$

Equation 62 calculation of χ for the [EMIM][MeSO₃] process

Table 37 values for Equation 25

	[EMIM][MeSO₃]	[EIM][NO₃]
Φ _{v,L} (m ³ /h)	14.453	14.453
Φ _{ν,н} (m³/h)	13.255	18.807
Φ _{v,Total} (m ³ /h)	26.877	32.692
φι	0.538	0.422
ρ _L (kg/m³)	697.9	697.9
ρ _н (kg/m³)	1242.4	1250.1
η₋ (Pa.s)	4.41*10 ⁻⁴	4.41*10 ⁻⁴
η _н (Pa.s)	0.135	0.116
x	5.45	3.25

G3 RDC design

Table 38 RDC configuration for [EMIM][MeSO₃]/thiophene/n-heptane/n-octane-system

Extraction section	[EMIM][MeSO₃]	[EIM][NO₃]
Stage height	0.7 m	0.7 m
Number of stages	10	10
Total height	7 m	7 m
Diameter column	0.7 m	0.7 m
Stator opening diameter	0.49 m	0.49 m
Rotor diameter	0.42 m	0.42 m
Stator thickness	0.02 m	0.02 m
Rotor thickness	0.02 m	0.02 m
Shaft diameter	0.10 m	0.10 m
Uc	0.0103 m/s	0.0103 m/s
U _d	0.0117 m/s	0.0150 m/s
Pressure drop stage	-5.5*10 ⁻² bar	-5.5*10 ⁻² bar
Total pressure drop	-0.55 bar	-0.52 bar
d32	0.79 mm	1.11 mm
φ _d	0.18	0.17
φ _f	0.34	0.36
Power rotor	170 W	170 W
Total power	1.7 kW	1.7 kW
N rotor	8.5 s ⁻¹ (510 RPM)	8.5 s ⁻¹ (510 RPM)
Nmin	0.46 RPS	0.55 RPS
ε	0.97	0.97
а	1348 m²/m³	978 m²/m³
uc	1.27*10 ⁻² m/s	1.27*10 ⁻² m/s
u _d	6.36*10 ⁻² m/s	8.05*10 ⁻² m/s
Settler section		
Height top settler	0.7 m	0.7 m
Diameter top settler	0.7 m	0.7 m
Height bottom settler	0.7 m	0.7 m
Diameter bottom settler	0.7 m	0.7 m
Pressure drop top settler	-5.5*10 ⁻² bar	-5.5*10 ⁻² bar
Pressure increase bottom settler	5.5*10 ⁻² bar	5.5*10 ⁻² bar
Overall		
Height	8.4 m	8.4 m
Pressure drop tower	-0.66 bar	-0.66 bar

G4 Distillation column design

Table 39 Distillation column design for RadFrac.

Specifications	[EMIM][MeSO₃]	[EIM][NO₃]	[EMIM][MeSO ₃]	[EIM][NO₃]
Operating regime	Vacu	um	atmosp	heric
Calculations Type	Equilibrium	Equilibrium	Equilibrium	Equilibrium
Number of stages	10	10	20	20
Number of trays	9	9	19	19
Condenser	Total	Total	Total	Total
Reboiler	Kettle	Kettle	Kettle	Kettle
Valid phases	Vapor-Liquid	Vapor-Liquid	Vapor-Liquid	Vapor-Liquid
Reflux ratio (mole)	8.94081	4.36626858	7.65877	5.28281
Distillate to feed ratio (mole)	0.00133431	0.0013889	0.00136	0.00140
Feed stage	6	6	13	12
Feed temperature (°C)	280	245	335	310
Condenser pressure (bar)	0.2	0.15	1	1
Tray rating				
Tray type	Bubble cap	Bubble cap	Bubble cap	Bubble cap
Tray diameter (m)	1.2	1.1	1.3	1.1
Tray spacing (m)	0.6069	0.6069	0.6069	0.6069
Number of passes (m)	1	1	1	1
Weir height	0.012	0.012	0.012	0.012
Flooding method	Fair72	Fair72	Fair72	Fair72
Bubble cap diameter (mm)	101.6	101.6	101.6	101.6
Skirt height (mm)	25.4	25.4	25.4	25.4
Cap spacing (cm)	3.81	3.81	3.81	3.81
Downcomer clearance (mm)	7	9	9	10
Downcomer width (m)	0.2	0.2	0.2	0.2
Results				
Condenser temperature (°C)	40.42	39.68	84.3	91.8
Condenser pressure (bar)	0.20	0.15	1	1
Condenser duty (kW)	-19.5	-16.8	-19.9	-21.8
Reboiler temperature (°C)	325.1	284.1	399.8	352.6
Reboiler pressure (bar)	0.26	0.22	1.12	1.12
Reboiler duty (kW)	971.6	997.5	1773.6	1198.8
Condenser pump duty (kW)	6.96*10 ⁻³	7.11*10 ⁻²	5.63*10 ⁻²	1.17*10 ⁻²
Steam conditions (in)	400°C, 40 bar	400°C, 40 bar	500°C, 50 bar	500°C, 50 bar
Steam conditions (out)	335°C, 40 bar	294°C, 40 bar	410°C, 50 bar	362°C, 50 bar



Figure 48 temperature and pressure profile inside the distillation column for the [EMIM][MeSO₃] system (vacuum)



Figure 49 temperature and pressure profile inside the distillation column for the [*EIM*][*NO*₃] *system (vacuum)*

G5 Economizer design

Table 40 Economizer specifications for the systems with distillation column at vacuum

Specifications	[EMIM][MeSO₃]	[EIM][NO₃]	[EMIM][MeSO₃]	[EIM][NO₃]
Operating regime	Vacuu	ım	atmosp	heric
Hot fluid	Shell side	Shell side	Shell side	Shell side
Flow direction	Counter-current	Counter-	Counter-current	Counter-
		current		current
TEMA shell type	F – Two-pass shell	F – Two-pass	F – Two-pass	F – Two-pass
		shell	shell	shell
Number of tube passes	2	2	2	2
Exchanger orientation	Horizontal	Horizontal	Horizontal	Horizontal
Inside shell diameter (m)	1.6	2.12	1.4	2.01
Shell to bundle clearance	95	95	95	95
(mm)				
Number of tubes	1399	2640	1020	2357
Pattern	Triangle	Triangle	Triangle	Triangle
Material	Copper	Copper	Copper	Copper
Tube length (m)	6.98	7.925	6.94	7.21
Pitch (mm)	37.5	37.5	37.5	37.5
Outer tube diameter	30	30	30	30
(mm)				
Tube thickness (mm)	2.1	2.1	2.1	2.1
Number of baffles	10	10	10	10
Baffle cut	0.25	0.25	0.25	0.25
Inlet and outlet nozzle	0.3	0.3	0.3	0.3
diameter for hot and				
cold side (m)				
Results				
Hot side temperature in	325	284	400	353
(°C)				
Hot side temperature out	124	75	189	85
(°C)				
Cold side temperature in	25	25	25	25
(°C)				
Cold side temperature	280	245	335	310
out (°C)				
ΔT_{m}	68.5	44.3	107	51.0
Heat transfer area (m ²)	920	1972	667	1601
Heat duty (kW)	3237	4717	4426	6387
Total pressure drop shell	3.79	0.26	18.7	0.29
side (mbar)				
Total pressure drop tube	2.73	1.31	3.51	1.30
side (mbar)				

H Mass balances

Table 41 Part 1 of mass balance for the [EMIM][MeSO₃] – vacuum system

Stream number	1	2	3	4	5	6	7	8	9	10	11	12	13
Temperature (°C)	25.00	25.00	25.00	25.00	25.01	280.08	280.00	156.39	40.42	40.42	40.42	40.42	40.42
Pressure (bar)	1.58	1.00	1.00	0.95	1.60	1.60	0.21	0.20	0.20	0.20	0.67	0.67	0.67
Vapor Frac	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.00	0.00	0.00	0.00	0.00	0.00
Mole Flow (kmol/h)	93.68	0.00	97.30	93.55	97.43	97.43	97.43	1.29	1.29	1.29	1.29	1.16	0.13
Mass Flow (kg/h)	10000.00	0.22	20070.00	9987.66	20082.34	20082.34	20082.34	124.79	124.79	124.79	124.79	112.24	12.55
Mass Flow (kg/h)													
n-heptane	4997.40	0.00	0.00	4993.33	4.07	4.07	4.07	40.46	40.46	40.46	40.46	36.39	4.07
n-octane	4997.40	0.00	0.00	4994.23	3.17	3.17	3.17	31.52	31.52	31.52	31.52	28.35	3.17
Thiophene	5.20	0.00	0.00	0.10	5.10	5.10	5.10	50.67	50.67	50.67	50.67	45.58	5.10
[EMIM][MeSO ₃]	0.00	0.22	20070.00	0.00	20070.00	20070.00	20070.00	2.14	2.14	2.14	2.14	1.92	0.22
Water	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mass Frac													
n-heptane	0.50	0.00	0.00	0.50	2.03E-04	2.03E-04	2.03E-04	0.32	0.32	0.32	0.32	0.32	0.32
n-octane	0.50	0.00	0.00	0.50	1.58E-04	1.58E-04	1.58E-04	0.25	0.25	0.25	0.25	0.25	0.25
Thiophene	5.20E-04	0.00	0.00	1.00E-05	2.54E-04	2.54E-04	2.54E-04	0.41	0.41	0.41	0.41	0.41	0.41
[EMIM][MeSO ₃]	0.00	1.00	1.00	0.00	1.00	1.00	1.00	0.02	0.02	0.02	0.02	0.02	0.02
Water	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table 42 Part 2 of mass balance for the [EMIM][MeSO₃] – vacuum system

14	15	16	17	18	19	20	21	22	23	24	25	26
322.56	325.11	325.11	325.17	123.68	25.00	20.00	25.00	400.00	335.00	20.00	25.00	N.A.
0.25	0.26	0.26	1.95	1.94	1.94	1.00	1.00	40.00	40.00	1.00	1.00	N.A.
0.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00	1.00	1.00	0.00	0.00	N.A.
138.58	41.28	97.30	97.30	97.30	97.30	186.70	186.70	1221.88	1221.88	9128.05	9128.05	0
28584.27	8514.49	20069.78	20069.78	20069.78	20069.78	3363.66	3363.66	22013.40	22013.40	164451.00	164451.00	0
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	N.A.
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	N.A.
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	N.A.
28584.27	8514.49	20069.78	20069.78	20069.78	20069.78	0.00	0.00	0.00	0.00	0.00	0.00	N.A.
0.00	0.00	0.00	0.00	0.00	0.00	3363.66	3363.66	22013.40	22013.40	164451.00	164451.00	N.A.
6.27E-30	6.27E-30	6.27E-30	6.27E-30	6.27E-30	6.27E-30	0.00	0.00	0.00	0.00	0.00	0.32	N.A.
1.55E-29	1.55E-29	1.55E-29	1.55E-29	1.55E-29	1.55E-29	0.00	0.00	0.00	0.00	0.00	0.25	N.A.
7.04E-14	7.04E-14	7.04E-14	7.04E-14	7.04E-14	7.04E-14	0.00	0.00	0.00	0.00	0.00	0.41	N.A.
1.00	1.00	1.00	1.00	1.00	1.00	0.00	0.00	0.00	0.00	0.00	0.02	N.A.
0.00	0.00	0.00	0.00	0.00	0.00	1.00	1.00	1.00	1.00	1.00	0.00	N.A.

Table 43 Part 1 of mass balance for the [EIM][NO₃] – vacuum system

Stream	1	2	3	4	5	6	7	8	9	10	11	12	13
number													
Temperature	25.00	25.0	25.00	25.00	25.00	245.06	244.91	106.01	39.68	39.68	39.68	39.68	39.68
(°C)		0											
Pressure (bar)	1.58	1.00	1.00	0.94	1.61	1.60	0.16	0.15	0.15	0.15	0.62	0.62	0.62
Vapor Frac	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.00	0.00	0.00	0.00	0.00	0.00
Mole Flow	93.68	0.00	163.55	93.46	163.78	163.78	163.78	1.22	1.22	1.22	1.22	0.99	0.23
(kmol/h)													
Mass Flow	10000.	0.05	26027.0	9976.46	26050.5	26050.5	26050.5	126.62	126.62	126.62	126.62	103.03	23.60
(kg/h)	00		0		4	4	4						
Mass Flow													
(kg/h)													
n-heptane	4997.4	0.00	0.00	4993.26	4.14	4.14	4.14	22.21	22.21	22.21	22.21	18.07	4.14
	0												
n-octane	4997.4	0.00	0.00	4983.09	14.31	14.31	14.31	76.78	76.78	76.78	76.78	62.47	14.31
	0	0.00	0.00	0.40	F 40	F 10	F 40	27.25	27.25	27.25	27.25	22.26	F 40
Iniophene	5.20	0.00	0.00	0.10	5.10	5.10	5.10	27.35	27.35	27.35	27.35	22.26	5.10
[EMIM][MeSO ₃]	0.00	0.05	26027.0	0.00	26027.0	26027.0	26027.0	0.28	0.28	0.28	0.28	0.23	0.05
	0.00	0.00	0	0.00	0	0	0	0.00	0.00	0.00	0.00	0.00	0.00
water	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mass Frac													
n-heptane	0.50	0.00	0.00	0.50	1.59E-04	1.59E-04	1.59E-04	0.18	0.18	0.18	0.18	0.18	0.18
n-octane	0.50	0.00	0.00	0.50	5.49E-04	5.49E-04	5.49E-04	0.61	0.61	0.61	0.61	0.61	0.61
Thiophene	5.20E-	0.00	0.00	1.00E-	1.96E-04	1.96E-04	1.96E-04	0.22	0.22	0.22	0.22	0.22	0.22
	04			05									
[EMIM][MeSO ₃]	0.00	1.00	1.00	0.00	1.00	1.00	1.00	2.24E-	2.24E-	2.24E-	2.24E-	2.24E-	2.24E-
								03	03	03	03	03	03
Water	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table 44 Part 2 of mass balance for the [EIM][NO₃] – vacuum system

14	15	16	17	18	19	20	21	22	23	24	25	26
280.95	284.09	284.09	284.17	75.46	25.00	20.00	25.00	400	294	20.00	25.00	N.A.
0.21	0.22	0.22	1.98	1.98	1.96	1.00	1.00	40	40	1.00	1.00	N.A.
0.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00	1.00	1.00	0.00	0.00	N.A.
210.32	46.77	163.55	163.55	163.55	163.55	160.74	160.74	732.93	732.93	9386.71	9386.71	0
33470.44	7443.49	26026.95	26026.95	26026.95	26026.95	2895.95	2895.95	13204.40	13204.40	169111.0	169111.00	0
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	N.A.
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	N.A.
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	N.A.
33470.44	7443.49	26026.95	26026.95	26026.95	26026.95	0.00	0.00	0.00	0.00	0.00	0.00	N.A.
0.00	0.00	0.00	0.00	0.00	0.00	2895.95	2895.95	13204.40	13204.40	169111.00	169111.00	N.A.
5.84E-30	5.84E-30	5.84E-30	5.84E-30	5.84E-30	5.84E-30	0.00	0.00	0.00	0.00	0.00	0.00	N.A.
9.20E-25	9.20E-25	9.20E-25	9.20E-25	9.20E-25	9.20E-25	0.00	0.00	0.00	0.00	0.00	0.00	N.A.
1.45E-13	1.45E-13	1.45E-13	1.45E-13	1.45E-13	1.45E-13	0.00	0.00	0.00	0.00	0.00	0.00	N.A.
1.00	1.00	1.00	1.00	1.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00	N.A.
0.00	0.00	0.00	0.00	0.00	0.00	1.00	1.00	1.00	1.00	1.00	1.00	N.A.

Table 45 Part 1 of mass balance for the [EMIM][MeSO₃] – atmospheric system

Stream	1	2	3	4	5	6	7	8	9	10	11	12	13
number													
Temperature	25.00	25.00	25.00	25.00	25.01	335.00	334.98	161.80	84.13	84.13	84.13	84.13	84.13
(°C)													
Pressure (bar)	1.58	1.00	1.00	0.95	1.60	1.60	1.02	1.00	1.00	1.00	1.92	1.92	1.92
Vapor Frac	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.00	0.00	0.00	0.00	0.00	0.00
Mole Flow	93.68	0.00	97.30	93.55	97.43	97.43	97.43	1.15	1.15	1.15	1.15	1.01	0.13
(kmol/h)													
Mass Flow	10000.00	0.05	20070.00	9987.32	20082.69	20082.69	20082.69	110.30	110.30	110.30	110.30	97.56	12.74
(kg/h)													
Mass Flow													
(kg/h)													
n-heptane	4997.40	0.00	0.00	4993.10	4.31	4.31	4.31	37.28	37.28	37.28	37.28	32.97	4.31
n-octane	4997.40	0.00	0.00	4994.11	3.29	3.29	3.29	28.51	28.51	28.51	28.51	25.22	3.29
Thiophene	5.20	0.00	0.00	0.11	5.09	5.09	5.09	44.05	44.05	44.05	44.05	38.96	5.09
[EMIM][MeSO ₃]	0.00	0.05	20070.00	0.00	20070.00	20070.00	20070.00	0.46	0.46	0.46	0.46	0.41	0.05
Water	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mass Frac													
n-heptane	0.50	0.00	0.00	0.50	2.14E-04	2.14E-04	2.14E-04	0.34	0.34	0.34	0.34	0.34	0.34
n-octane	0.50	0.00	0.00	0.50	1.64E-04	1.64E-04	1.64E-04	0.26	0.26	0.26	0.26	0.26	0.26
Thiophene	5.20E-04	0.00	0.00	1.10E-05	2.53E-04	2.53E-04	2.53E-04	0.40	0.40	0.40	0.40	0.40	0.40
[EMIM][MeSO ₃]	0.00	1.00	1.00	0.00	1.00	1.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00
Water	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

14	15	16	17	18	19	20	21	22	23	24	25	26
399.08	399.78	399.78	399.80	189.64	25.00	20.00	25.00	500.00	410.00	20.00	25.00	N.A.
1.10	1.11	1.11	1.94	1.92	1.92	1.00	1.00	50.00	50.00	1.00	1.00	N.A.
0.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00	1.00	1.00	0.00	0.00	N.A.
185.16	87.86	97.30	97.30	97.30	97.30	141.57	141.57	1670.83	1670.83	16813.06	16813.06	0
38191.75	18121.80	20069.95	20069.95	20069.95	20069.95	2550.60	2550.60	30101.60	30101.60	302904.00	302904.00	0
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	N.A.
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	N.A.
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	N.A.
38191.76	18121.81	20069.95	20069.95	20069.95	20069.95	0.00	0.00	0.00	0.00	0.00	0.00	N.A.
0.00	0.00	0.00	0.00	0.00	0.00	2550.60	2550.60	30101.60	30101.60	302904.00	302904.00	N.A.
5.45E-43	5.45E-43	5.45E-43	5.45E-43	5.45E-43	5.45E-43	0.00	0.00	0.00	0.00	0.00	0.00	N.A.
1.26E-42	1.26E-42	1.26E-42	1.26E-42	1.26E-42	1.26E-42	0.00	0.00	0.00	0.00	0.00	0.00	N.A.
3.20E-19	3.20E-19	3.20E-19	3.20E-19	3.20E-19	3.20E-19	0.00	0.00	0.00	0.00	0.00	0.00	N.A.
1.00	1.00	1.00	1.00	1.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00	N.A.
0.00	0.00	0.00	0.00	0.00	0.00	1.00	1.00	1.00	1.00	1.00	1.00	N.A.

Table 46 Part 2 of mass balance for the [EMIM][MeSO₃] – atmospheric system

Table 47 Part 1 of mass balance for the $[EIM][NO_3]$ – atmospheric system

Stream	1	2	3	4	5	6	7	8	9	10	11	12	13
number													
Temperature	25.00	25.0	25.00	25.00	25.00	310.01	309.96	185.58	91.83	91.83	91.83	91.83	91.83
(°C)		0											
Pressure (bar)	1.58	1.00	1.00	0.94	1.61	1.60	1.04	1.00	1.00	1.00	1.47	1.47	1.47
Vapor Frac	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.00	0.00	0.00	0.00	0.00	0.00
Mole Flow	93.68	0.00	163.55	93.46	163.78	163.78	163.78	1.44	1.44	1.44	1.44	1.21	0.23
(kmol/h)													
Mass Flow	10000.0	0.34	26027.0	9976.4	26050.5	26050.5	26050.5	150.07	150.07	150.07	150.07	126.18	23.89
(kg/h)	0		0	6	4	4	4						
Mass Flow													
(kg/h)													
n-heptane	4997.40	0.00	0.00	4993.2	4.14	4.14	4.14	26.00	26.00	26.00	26.00	21.87	4.14
				6									
n-octane	4997.40	0.00	0.00	4983.0	14.31	14.31	14.31	89.89	89.89	89.89	89.89	75.58	14.31
				9									
Thiophene	5.20	0.00	0.00	0.10	5.10	5.10	5.10	32.03	32.03	32.03	32.03	26.93	5.10
[EMIM][MeSO	0.00	0.34	26027.0	0.00	26027.0	26027.0	26027.0	2.15	2.15	2.15	2.15	1.81	0.34
3]			0		0	0	0						
Water	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mass Frac													
n-heptane	0.50	0.00	0.00	0.50	1.59E-04	1.59E-04	1.59E-04	1.73E-	1.73E-	1.73E-	1.73E-	1.73E-	1.73E
								01	01	01	01	01	-01
n-octane	0.50	0.00	0.00	0.50	5.49E-04	5.49E-04	5.49E-04	5.99E-	5.99E-	5.99E-	5.99E-	5.99E-	5.99E
								01	01	01	01	01	-01
Thiophene	5.20E-04	0.00	0.00	1E-05	1.96E-04	1.96E-04	1.96E-04	2.13E-	2.13E-	2.13E-	2.13E-	2.13E-	2.13E
								01	01	01	01	01	-01
[EMIM][MeSO	0.00	1.00	1.00	0.00	1.00	1.00	1.00	1.43E-	1.43E-	1.43E-	1.43E-	1.43E-	1.43E
3]								02	02	02	02	02	-02
Water	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table 48 Part 2 of mass balance for the [EIM][NO₃] – atmospheric system

14	15	16	17	18	19	20	21	22	23	24	25	26
352.04	352.61	352.61	352.64	85.24	25.00	20.00	25.00	500	363	20.00	25.00	N.A.
1.11	1.12	1.12	1.95	1.94	1.94	1.00	1.00	50	50	1.00	1.00	N.A.
0.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00	1.00	1.00	0.00	0.00	N.A.
235.49	71.94	163.55	163.55	163.55	163.55	208.53	208.53	728.59	728.59	11258.88	11258.88	0
37475.56	11448.90	26026.66	26026.66	26026.66	26026.66	3756.79	3756.79	13126.20	13126.20	202840.0	202840.00	0
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	N.A.
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	N.A.
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	N.A.
37475.59	11448.93	26026.66	26026.66	26026.66	26026.66	0.00	0.00	0.00	0.00	0.00	0.00	N.A.
0.00	0.00	0.00	0.00	0.00	0.00	3756.79	3756.79	13126.20	13126.20	202840.00	202840.00	N.A.
3.11E-47	3.11E-47	3.11E-47	3.11E-47	3.11E-47	3.11E-47	0.00	0.00	0.00	0.00	0.00	0.00	N.A.
2.93E-39	2.93E-39	2.93E-39	2.93E-39	2.93E-39	2.93E-39	0.00	0.00	0.00	0.00	0.00	0.00	N.A.
4.19E-20	4.19E-20	4.19E-20	4.19E-20	4.19E-20	4.19E-20	0.00	0.00	0.00	0.00	0.00	0.00	N.A.
1.00	1.00	1.00	1.00	1.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00	N.A.
0.00	0.00	0.00	0.00	0.00	0.00	1.00	1.00	1.00	1.00	1.00	1.00	N.A.

I heat balance

Table 49 Heat exchanger area and pressure drop over E4 and E1

Process	Area (m²) E4	Pdrop E1 (mbar)	Pdrop E4 (mbar)	Discharge Pressure P2 (bar)
[EMIM][MeSO ₃] vacuum	566	3.79	2.34	1.945
[EIM][NO₃] vacuum	926	18.7	16.3	1.979
[EMIM][MeSO ₃]	583	0.26	0.12	1.939
atmospheric				
[EIM][NO ₃] atmospheric	672	0.29	0.12	1.945

Table 50 Heat transfer areas for E2 and E3, which are used in the economic analysis

Area (m²)	[EMIM][MeSO ₃] [EIM][NO ₃]		[EMIM][MeSO ₃]	[EIM][NO₃]
Operating regime	Vacuum		Atmospheric	
C2				
E2	0.47	0.55	0.22	0.28
E3	39.91	42.25	87.73	44.80

J Economical analysis

Table 51 Various pressure of steam, with their specifications and price (Sinnott & Towler, 2013g) (SUPERHP and SUPERMP for high pressure and medium pressure in Figure 34)

	Extra high pressure	High	pressure	Medium	Pressure	Low Pressure
Pressure (Bar)	50	40		20		6
Saturation	264	250		212		159
temperature (°C)						
Superheat	500	400		300		160
temperature (°C)						
Specific Enthalpy	3433	3214		3025		2757
(kJ/kg)						
Shaft work credit	219		1.02	1		1.44
(\$/Mlb)						
Steam price	7.65	6.48		5.47		4.03
(\$/Mlb)						
Steam price	15.69	13.29		11.22		8.26
(€/ton) (0.93 €/\$)						

Equipment Cost (\$/h)	Utility type	[EMIM][MeSO₃]	[EIM][NO₃]	[EMIM][MeSO₃]	[EIM][NO₃]
Operating regime C2		Vacuum		Atmospheric	
C1	Electric	0.13	0.13	0.13	0.13
E2	Cooling water	0.01	0.01	0.01	0.02
E3	High pressure steam	314.48	188.64	507.67	221.38
E4	Cooling water	0.73	0.75	1.34	0.90
P1	Electric	0.00	0.01	0.00	0.02
P2	Electric	0.52	0.16	0.77	0.08
Total		315.88	189.69	509.93	222.52

Table 52 Hourly cost of different equipment pieces for all four different processes (obtained from Aspen Plus)

Table 53 The Equipment cost, including Hand's Installation factor (Sinnott & Towler, 2013a).

Equipment cost (\$)	Hand's Installation factor	[EMIM][MeSO₃]	[EIM][NO₃]	[EMIM][MeSO₃]	[EIM][NO₃]
Operating regime C2		Vacuum		Atmospheric	
C1	2.5	309,750.00	309,750.00	309,750.00	309,750.00
C2	4	348,400.00	330,800.00	1,170,000.00	869,200.00
E1	3.5	1,425,200.00	2,890,650.00	1,070,300.00	2,390,850.00
E2	3.5	28,350.00	28,350.00	26,600.00	26,600.00
E3	3.5	79,100.00	88,200.00	122,150.00	89,950.00
E4	3.5	808,500.00	1,240,050.00	827,400.00	937,300.00
P1	4	17,600.00	17,600.00	17,600.00	17,600.00
P2	4	25,600.00	28,000.00	25,200.00	28,400.00
Р3	4	25,600.00	28,000.00	25,200.00	28,400.00
V1	4	12,800.00	12,800.00	12,800.00	12,800.00
T1	2.5	160,000.00	160,000.00	160,000.00	160,000.00
Total		3.080.900,00	4.974.200,00	3.607.000,00	4.710.850,00
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