

# Separation of Methylcyclohexane–Toluene Mixture Using Imidazolium Ionic Liquids

Elena Graczová\*, Dávid Molnár, Pavol Steltenpohl

Institute of Chemical and Environmental Engineering, Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Radlinského 9, 812 37 Bratislava, Slovakia  
[elena.graczova@stuba.sk](mailto:elena.graczova@stuba.sk)

This study aimed to design a process for methylcyclohexane–toluene mixture separation. For the separation of a binary mixture containing 10 mole % of toluene, two imidazolium ionic liquids (ILs) were tested, namely 1-hexyl-3-methylimidazolium tetracyanoborate [Hmim][TCB] and 1-butyl-3-methylimidazolium tetracyanoborate [Bmim][TCB]. These ILs were chosen to substitute traditional solvents, such as *N*-methyl-2-pyrrolidone, sulfolane or glycols, to minimize the content of extraction solvent in the separation products and to optimize the separation process expenditures.

A separation unit composed of a counter-current extraction column, vacuum evaporator and a vacuum distillation column was suggested for the process. Prescribed efficiency of the separation units was as follows: minimum methylcyclohexane of 99.5 mole % in the raffinate phase in the extraction column, ionic liquid purity regenerated in vacuum evaporator above 99 mole %, and minimum toluene purity leaving the bottom of the vacuum distillation column of 99.5 mol%.

Simulation of the counter-current extraction column was carried out in Matlab. Operation of the remaining separation equipment was simulated using the Aspen Plus program which allowed evaluation of the energetic requirements of the proposed separation unit. It was found that both ionic liquids ([Hmim][TCB] and [Bmim][TCB]) are almost equally appropriate for this task. A comparison of energy consumption of the process using each ionic liquid was done. For [Hmim][TCB], heat integration of the separation unit was accomplished. Employing a part of the heat content of the regenerated solvent for extract stream preheating, significantly reduced unit energy consumption (by about 72 %).

## 1. Introduction

Aromatic hydrocarbons such as benzene, toluene, ethylbenzene, and xylene (BTX fractions) are important products of petroleum processing and have a wide application in the chemical and especially in the petrochemical industry. In addition, they are high-octane components of gasoline which increase the quality of the final products (Aromatics Producers' Association, 2022). At present, the toluene-methylcyclohexane mixture is of increased interest (Papadias & Ahluwalia, 2021) as it is tested as a carrier for hydrogen transmission (Akram & Usman, 2021).

Feedstock entering the ethylene unit, depending on whether it is naphtha or gas fractions, contains 10 to 25 mass % of aromatic hydrocarbons on average. Aromatics are undesirable substances in the ethylene producing unit because they occupy a large part of the furnaces thus reducing their capacity and thermal efficiency. Another disadvantage of the presence of aromatics in the pyrolysis unit is that they largely cause coking, i.e., kiln fouling. For these reasons, separation of aromatics from the ethylene unit feedstock is important even before they enter the pyrolysis furnaces. In this case, overall capacity and thermal efficiency of the kiln increases and the coking rate of the plants decreases (Meindersma & de Haan, 2008). Difficult separation of aromatics from aliphatic hydrocarbons is due to the close boiling points these substances and the formation of azeotropic mixtures of individual components. The conventionally and commonly used method for the separation of mixtures with the aromatics content in the range of 20-65 mass % is liquid extraction. Extractive distillation is generally suitable for the separation of mixtures with aromatics content in

the range of 65–90 mass %, while mixtures with high content of aromatic hydrocarbons (more than 90 mass %) are separated by azeotropic distillation (Meindersma et al., 2010).

The most frequently used extraction solvents for aromatics separation are NMP, sulfolane, dimethyl sulfoxide, ethylene glycol, etc (Canales & Brennecke, 2016). However, their regeneration is often energy and investment intensive and there is an increasing effort to replace traditional organic solvents with modern ones - ionic liquids. The main advantage of ionic liquids is that they are liquid salts and their saturated vapor pressure is negligibly low which ensures easier solvent regeneration and provides solvent-free separation products. Another advantage of ILs is that their properties can be altered by changing the functional groups in their cation or anion (Perriero et al., 2012). High selectivity of the studied ILs towards the original mixture components allows minimizing the number of down-stream processing steps, e.g., regeneration of extraction solvent from the raffinate is not necessary and thus unit investment and operation costs can be reduced. Therefore, ionic liquids are suitable to replace conventional organic solvents not only in the process of aromatics separation from petroleum fractions but also in other processes of the chemical industry.

Superiority of ionic liquids over conventional organic solvents dwells in their non-flammability, non-volatility, and their relatively simple regeneration. Ionic liquids are liquid over a wide temperature range, with a melting point below 100 °C, which allows better control over the process kinetics. Many ionic liquids are non-toxic, have no negative impact on the environment and so do not pose any environmental risk. Thanks to their advantageous properties, they are included among the so-called "Green solvents" (Ghandi, 2014).

For the separation of a toluene–methylcyclohexane mixture by extraction or extractive distillation, various ILs were tested: 1-ethyl-3-methylpyridinium ethylsulfate (González et al., 2010), 1-ethyl-3-methylimidazolium ethylsulfate (González et al., 2011), 1-hexyl-3-methylimidazolium tetracyanoborate and 1-butyl-3-methylimidazolium tetracyanoborate (Gutiérrez et al., 2011). Gutiérrez et al. (2012) used a solvent selection methodology (COSMO-RS, conductor-like screening model) to test 12 ILs for extractive distillation of a toluene–methylcyclohexane mixture. The authors found that tetracyanoborate anion-based ILs (1-hexyl-3-methylimidazolium tetracyanoborate and 1-butyl-3-methylimidazolium tetracyanoborate) are promising solvents for the separation of this mixture by extractive distillation. Based on systematic methodology for screening and designing of (IL)-based separation processes, two ionic liquids ([bmim] and [hmim] tetracyanoborate ILs) for toluene–methylcyclohexane mixture separation were selected by Peng-noo et al. (2015).

More effort has recently been invested in improving energy-demanding technologies based on liquid–liquid extraction (Quijada-Maldonado et al., 2016) and extractive distillation processes (Quijada-Maldonado et al., 2018). Ionic liquid-based technologies for the separation of benzene, toluene, and xylene from pyrolysis gasoline have been evaluated, and extractive distillation showed more potential than the liquid–liquid extraction in terms of separation performance and global energy requirements (Ayuso et al., 2022).

The presented work aims to design a process of methylcyclohexane–toluene mixture separation in the presence of ionic liquids. Based on the literature, two tetracyanoborate-based ILs were selected. Besides the simulation of the separation unit operation, a part of the work was aimed to evaluate the energy demands of the separation unit for both chosen ILs.

## 2. Phase equilibrium of ternary systems

Liquid–liquid equilibrium (LLE) of the ternary system was expressed by the isoactivity criterion; vapor–liquid equilibrium (VLE) was expressed by the extended Raoult's law assuming ideal behavior of vapor and real behavior of liquid phases. Activity coefficients of components,  $\gamma_i$ , were calculated using the original NRTL model (Renon & Prausnitz, 1968). A, B and C represent the mixture components.

## 3. Selection of ionic liquids

In this work, two ionic liquids suitable for the separation of aromatics from aliphatic hydrocarbons by extraction were applied: 1-hexyl-3-methylimidazolium tetracyanoborate ([Hmim][TCB]); 1-butyl-3-methylimidazolium tetracyanoborate ([Bmim][TCB]).

### 3.1 Physical properties

Saturated vapor pressure variation with temperature ( $P_i^o = f(T)$ ) for methylcyclohexane and toluene is well known. For [Bmim][TCB] and [Hmim][TCB], this relation is not known. In simulations, saturated vapor pressures of these ILs were assumed to be zero. Published experimental values of saturated vapor pressure for [Hmim][TCB] in the temperature range from 115 °C to 153 °C (Zaitsau et al., 2017) are negligibly low (of the order of  $10^{-9}$  kPa to  $10^{-7}$  kPa). Then, the assumption of a zero saturated vapor pressure of chosen ILs is reasonable.

Temperature dependence of the isobaric heat capacity of ionic liquids was predicted using the contribution method of Chueh and Swanson (1973). Temperature variation of heat capacity values for methylcyclohexane (MCH) and toluene (Tol) is readily available in literature, as well as the temperature dependence of the heat of vaporization of these substances.

To avoid problems of LLE description (Graczová et al., 2015), parameters of NRTL equation of the studied systems were recalculated from the experimental data published by Gutierrez et al. (2011) using minimization of the objective function based on the isoactivity criterion. Results are presented in Table 1.

*Table 1: Binary parameters of the NRTL equation*

Components $i-j$	$\tau_{ij}$	$\tau_{ji}$	$\alpha_{ij}$
MCH–Tol	–0.1475	0.4573	0.300
MCH–[Bmim][TCB]	10.4000	1.6536	0.200
Tol–[Bmim][TCB]	7.0783	–2.1520	0.200
MCH–[Hmim][TCB]	7.0459	0.7064	0.200
Tol–[Hmim][TCB]	7.0664	–2.4431	0.200

#### 4. Separation process

The mixture to be separated contained 90 mole % of methylcyclohexane and 10 mole % of toluene and the separation was designed for 10 kmol h<sup>–1</sup> of feed entering the extractor. The separation unit consisted of three principal apparatuses: counter-current extraction column, vacuum evaporator, and vacuum distillation column. The aim was to design a counter-current extraction column for the separation of a methylcyclohexane–toluene mixture with ionic liquid ([Hmim][TCB] or [Bmim][TCB]) extractant so that the purity of MCH in the raffinate is 99.5 mole %; vacuum evaporator operating conditions at which the purity of the recovered IL leaving the vacuum evaporator is 99 mole %; and such vacuum distillation column operation parameters to achieve the purity of toluene leaving the bottom of the distillation column of at least 99.5 mole %.

##### 4.1 Design of separation unit

A unit for the separation of feed, methylcyclohexane–toluene mixture, including the regeneration of an extraction solvent, ionic liquid, was proposed and its operation was designed. The unit consists of an extractor (EC), which uses ionic liquids to separate the feed into raffinate R and extract E. The raffinate contains mainly methylcyclohexane (a minimum of 99.5 mole %) while the extract contains predominantly ionic liquid, the extracted component (toluene) and a small amount of methylcyclohexane. This mixture further passes through a throttle valve (V1) to enter the vacuum evaporator (EVAP), where the extraction solvent is regenerated. Operating conditions (pressure and temperature) in the evaporator are set according to the required purity of the regenerated ionic liquid. Vapor leaving the evaporator, stream D1, containing only methylcyclohexane and toluene, is condensed and cooled down in the heat exchanger (C1) and then it enters the vacuum distillation column (RC). The bottom product of this column, stream W2, contains toluene with the purity of 99.8 mole %. Distillate from the column, stream D2, containing methylcyclohexane and toluene, is mixed with fresh feed, F, and enters the extraction column (EC). The liquid phase leaving the evaporator (stream W1, containing regenerated solvent with traces of methylcyclohexane and toluene) is returned to the head of the extraction column (EC) after cooling in the heat exchanger (C2). Flow sheet of the unit for methylcyclohexane–toluene mixture separation by extraction using ionic liquid [Hmim][TCB] is presented in Figure 1.

##### 4.2 Simulation of extraction column operation

Simulations of the counter-current extractor operation were carried out using the Matlab program as presented elsewhere (Graczová et al., 2013). The extractor model is based on the mass balance equations integrated with the phase equilibrium description. Extraction process was assumed to be isothermal ( $t = 20$  °C), as the thermal effect of the liquids' mixing was neglected. Operation of the remaining separation equipment was simulated using the Aspen Plus program that allows evaluation of the energetic requirements of the proposed separation unit. In Aspen Plus, the extractor was modeled as a component separator block.

Data obtained in Matlab were used as the input data for the component separator block in Aspen Plus. Simulation results accomplished in Aspen Plus without switching one the recycle connections, were subsequently used as a new input for the calculations in Matlab. Using multiple iteration steps (manually altering computations in Matlab and in Aspen Plus), steady state conditions of the separation unit operation were reached.

Comparison of the results obtained for the proposed counter-current extraction column using two ionic liquids in terms of the number of theoretical contacts,  $N$ , and the minimum and the real amount of extractant used,

$\dot{n}_{Smin}$  and  $\dot{n}_S$ , resp., is given in Table 2. Purity of both regenerated ionic liquids ([Bmim][TCB] and [Hmim][TCB]) was 99 mole %.

Table 2: Operation conditions and parameters of the proposed counter-current extraction column,  $t = 20\text{ }^\circ\text{C}$

System	$\dot{n}_{Smin}/(\text{kmol h}^{-1})$	$\dot{n}_S/(\text{kmol h}^{-1})$	$x_{F1,Tol}$	$N$
MCH-Tol-[Bmim][TCB]	6.459	8.397	0.1343	12
MCH-Tol-[Hmim][TCB]	5.298	6.887	0.1354	13

\* $\dot{n}_{Smin} = 1.3\dot{n}_S$

Composition of the feed entering the extractor,  $x_{F1}$ , varies depending on the composition of the distillate (D2) of the distillation column (RC).

#### 4.3 Design of vacuum evaporator operation

Setting the appropriate temperature and pressure in the evaporator (EVAP) is a key step in designing the regeneration part of the separation unit. To avoid ILs decomposition in the evaporator (decomposition temperature of about  $170\text{ }^\circ\text{C}$  for both ILs (Gutiérrez-Hernández, 2013)), the pressure was set to 3.5 kPa and temperature to  $160\text{ }^\circ\text{C}$ . At these conditions, ionic liquid purity of 99 mole % in the liquid phase (W1) was achieved for both considered ionic liquids. Vapors leaving the evaporator (D1) are a two-component mixture of methylcyclohexane and toluene and contain 33 mole % to 43 mole % of methylcyclohexane.

#### 4.4 Design of distillation column operation

Vapors leaving the evaporator head (D1) proceed to the vacuum distillation column (RC), where the main product (toluene) leaves the bottom with the purity of 99.8 mole %. Distillate (D2) from RC is a two-component methylcyclohexane–toluene mixture which is returned to the extraction column (EC) after it is mixed with fresh feed (F). The yield of toluene in the distillation column (stream W2) is about 65 % with respect to toluene amount in stream D1. Table 3 shows the calculated optimal distillation column parameters and conditions for both ionic liquids used. It is obvious that the values of the minimum reflux ratio are relatively high. This is due to the low relative volatility of the methylcyclohexane–toluene mixture despite the low pressure (3.5 kPa).

Table 3: Operation conditions and parameters of the proposed distillation column

System	$N$	$f$	$R_{min}$	$R$
MCH-Tol-[Bmim][TCB]	18	6	1.97	2.45
MCH-Tol-[Hmim][TCB]	18	6	1.80	2.24

#### 4.5 Material and energy balances of the separation unit

Material balances of individual equipment included in the separation unit were evaluated. A scheme of this unit for the methylcyclohexane–toluene separation using ILs is presented in Figure 1, which also contains information on the molar flow, composition, pressure, and temperature of individual process streams (namely for the ionic liquid [Hmim][TCB]).

Results of the process energy analysis are presented in Table 4. The highest heat demand is associated with the vacuum evaporator (EVAP) operation where evaporation of the mixture at  $160\text{ }^\circ\text{C}$ , in case of both ILs ([Bmim][TCB] and [Hmim][TCB]), occurs. Heat is also consumed in the boiler of the vacuum distillation column (RC), but the required amount of heat is by an order of magnitude lower than that in the evaporator (EVAP). Moreover, high pressure steam is used for heating in the evaporator, while steam at atmospheric pressure can be used as a heating medium in the reboiler of the RC column. The largest demand for cooling medium is associated with the cooler of recirculated ionic liquid (C2). In this heat exchanger, regenerated ionic liquid is cooled from the evaporator temperature of  $160\text{ }^\circ\text{C}$  to  $20\text{ }^\circ\text{C}$ .

Thermal integration of the separation unit enables reducing the consumption of energy media such as heating steam and cooling water. Pinch point analysis was used to construct the composition curves, which were used to identify the maximum amount of heat that can be recovered and the necessary amount of heating/cooling media. Results of the pinch point analysis and the resulting thermal integration of the unit show that the actual amount of heat recovered in the process (158.1 kW) represents a reduction in the process energy requirements by approximately 71.5 %.

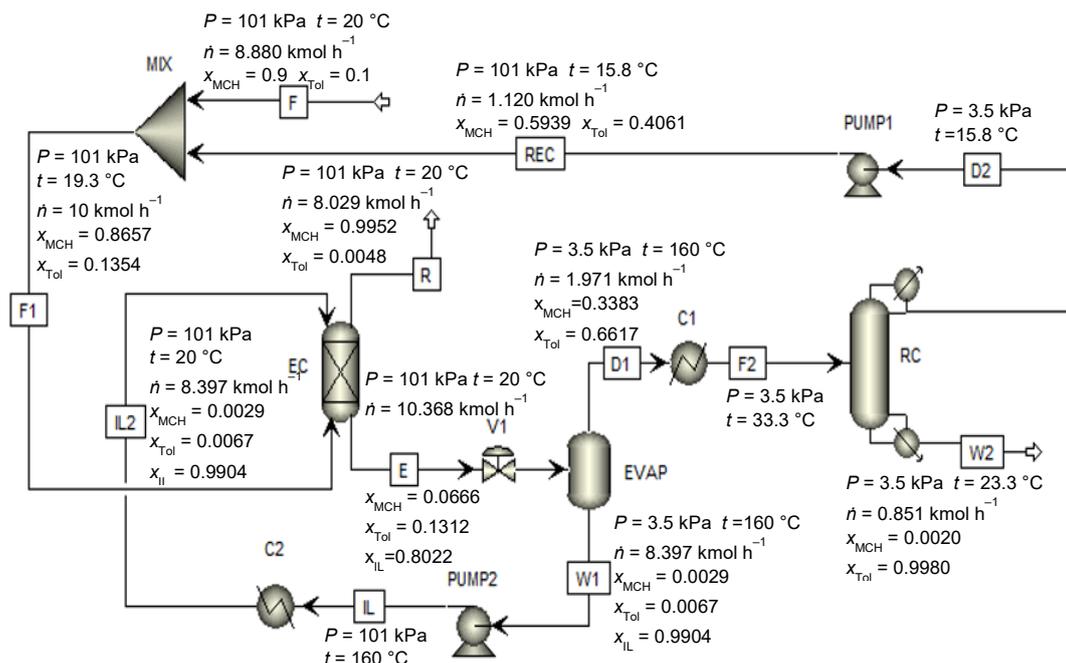


Figure 1: Final flowsheet for the separation of methylcyclohexane–toluene mixture by liquid extraction using ionic liquid [Hmim][TCB] as extraction solvent

Table 4: Results of the unit energy analysis,  $\dot{Q}$  in kW

Equipment	MCH–Tol–[Bmim][TCB]	MCH–Tol–[Hmim][TCB]
Heating of evaporator (EVAP)	201.25	196.97
Reboiler of distillation column (RC)	19.40	25.29
Condenser of distillation column (RC)	–39.10	–47.10
Heat exchanger (C1)	–10.21	–11.88
Heat exchanger (C2)	–170.09	–161.56
Total heating power	220.65	222.26
Total cooling power	–219.40	–220.54

## 5. Conclusions

In this study, a separation unit for methylcyclohexane–toluene mixture separation using a ionic liquid as the extraction solvent was designed. Two ionic liquids containing the same tetracyanoborate anion ([Bmim][TCB] and [Hmim][TCB] were compared. The separation process was designed to run in a continuously operated extractor with a regeneration part consisting of a vacuum evaporator and a vacuum distillation column. The use of selective extraction solvents allowed obtaining high purity solvent-free products. Furthermore, extraction solvent regeneration was carried out from one of the streams from the extractor, which minimizes the separation unit energy demand.

Design calculations of the extraction column provided the optimum number of theoretical stages and solvent demand. From the point of view of the extraction solvent demand, [Hmim][TCB] appears to be slightly more advantageous. Suitable operating conditions in the vacuum evaporator were determined for both ILs considered as: pressure of 3.5 kPa, temperature of 160 °C. Design calculations of the vacuum distillation column were focused on the optimal operation parameters and conditions (number of theoretical stages, feed stage position, reflux ratio) revealing [Hmim][TCB] as a more suitable solvent also in this regard. For [Hmim][TCB], heat integration of the separation unit was accomplished. It was found that it is possible to achieve significant savings in energy media consumption in the separation unit and, thus, to reduce the unit operating costs by almost 72 %.

It is worth investigating the effect of other ionic liquids as extraction solvents for MCH separation from its mixture with toluene in order to minimize process expenditures.

## Acknowledgments

This work was supported by the Research and Development Assistance Agency APVV (APVV-18-232).

## References

- Ayuso M., Navarro P., Moya C., Moreno D., Palomar J., Garcia J., Rodríguez F., 2022, Extractive distillation with ionic liquids to separate benzene, toluene, and xylene from pyrolysis gasoline: Process design and techno-economic comparison with the morphylane process, *Industrial & Engineering Chemistry Research*, 61(6), 2511–2523.
- Akram M.S., Usman M.R., 2021, Simulation and optimization of hydrogen fueled mobile power plant based on methylcyclohexane–toluene–hydrogen cycle, *Theoretical Foundations of Chemical Engineering*, 55, 545–561.
- Aromatics Producers' Association, 2022, Aromatics, Petrochemicals Europe <<https://www.petrochemistry.eu/sector-group/aromatics/>> accessed 17.03.2022.
- Canales R.I., Brennecke J.F., 2016, Comparison of ionic liquids to conventional organic solvents for extraction of aromatics from aliphatics, *Journal of Chemical & Engineering Data*, 61(5), 1685–1699.
- Chueh C.F., Swanson A.C., 1973, Estimation of liquid heat capacity, *The Canadian Journal of Chemical Engineering*, 51(5), 596–600.
- Ghandi K., 2014, A review of ionic liquids, their limits and applications, *Green and Sustainable Chemistry*, 4, 44–53.
- González E.J., Calvar N., Canosa J., Domínguez Á., 2010, Effect of the chain length on the aromatic ring in the separation of aromatic compounds from methylcyclohexane using the ionic liquid 1-ethyl-3-methylpyridinium ethylsulfate, *Journal of Chemical & Engineering Data*, 55(6), 2289–2293.
- González E.J., Calvar N., Gómez E., Domínguez Á., 2011, Application of [EMim][ESO<sub>4</sub>] ionic liquid as solvent in the extraction of toluene from cycloalkanes: Study of liquid–liquid equilibria at  $T = 298.15$  K, *Fluid Phase Equilibria*, 303(2), 174–179.
- Gracová E., Steltenpohl P., Šoltýs M., Katriňák T., 2013, Design calculations of an extractor for aromatic and aliphatic hydrocarbons separation using ionic liquids, *Chemical Papers*, 67(12), 1548–1559.
- Gracová E., Steltenpohl P., Labovský J., 2015, Incorrect ternary liquid–liquid equilibria description versus extractor design simulation, *Chemical Engineering Transactions*, 45, 1963–1968.
- Gutiérrez J.P., Meindersma W., de Haan A.B., 2011, Binary and ternary (liquid + liquid) equilibrium for {methylcyclohexane (1) + toluene (2) + 1-hexyl-3-methylimidazolium tetracyanoborate (3)/1-butyl-3-methylimidazolium tetracyanoborate (3)}, *The Journal of Chemical Thermodynamics*, 43, 1672–1677.
- Gutiérrez J.P., Meindersma G.W., de Haan A.B., 2012, COSMO-RS-based ionic-liquid selection for extractive distillation processes, *Industrial & Engineering Chemistry Research*, 51(35), 11518–11529.
- Gutiérrez-Hernández J.P., 2013, Extractive distillation with ionic liquids as solvents: selection and conceptual process design, PhD Thesis, Eindhoven University of Technology, Eindhoven, The Netherlands.
- Meindersma G.W., de Haan A.B., 2008, Conceptual process design for aromatic/aliphatic separation with ionic liquids, *Chemical Engineering Research and Design*, 86, 745–752.
- Meindersma G.W., Hansmeier A.R., de Haan A.B., 2010, Ionic liquids for aromatics extraction. Present status and future outlook, *Industrial & Engineering Chemistry Research*, 49(16), 7530–7540.
- Papadias D.D., Ahluwalia R.K., 2021, Toluene-methylcyclohexane as two-way carrier for hydrogen transmission and storage. Final CRADA Report ANL/ES-C2021-19122. Energy Systems, Argonne National Laboratory, Lemont, IL, USA.
- Peng-noo W., Kulajanpeng K., Gani R., Suriyapraphadilok U., 2015, Design of separation processes with ionic liquids, *Computer Aided Chemical Engineering*, 37, 1325–1330.
- Pereiro A.B., Araújo J.M.M., Esperanca J.M.S.S., Marrucho I.M., Rebelo L.P.N., 2012, Ionic liquids in separations of azeotropic systems – A review, *The Journal of Chemical Thermodynamics*, 46, 2–28.
- Quijada-Maldonado E., Meindersma G.W., de Haan A.B., 2016, Pilot plant study on the extractive distillation of toluene–methylcyclohexane mixtures using NMP and the ionic liquid [hmim][TCB] as solvents, *Separation and Purification Technology*, 166, 196–204.
- Quijada-Maldonado E., Meindersma G.W., de Haan A.B., 2018, Mass transfer in extractive distillation when using ionic liquids as solvents, Chapter 6 In: Y. Ren (Ed.) *Heat and Mass Transfer - Advances in Modelling and Experimental Study for Industrial Applications*, IntechOpen, London, UK, 724–777.
- Renon H., Prausnitz J.M., 1968, Local compositions in thermodynamic excess functions for liquid mixtures, *AIChE Journal*, 14(1), 135–144.
- Zaitsau D.H., Póhako-Esko K., Arlt S., Emel'yanenko V.N., Schulz P., Wasserscheid P., Schulz A., Verevkin S., 2017, Thermodynamics of imidazolium based ionic liquids with cyano containing anions, *Journal of Molecular Liquids*, 248, 86–90.