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Optimal Design of Extraction-Distillation Hybrid Processes by Combining Equilibrium and Rate-Based Modeling

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ABSTRACT

Liquid-liquid extraction (LLX) is an essential technique for separating heat-sensitive, highly diluted, or azeotropic mixtures. However, the design and optimization of LLX processes can be challenging due to mass transfer limitations and complex fluid dynamics. While distillation can often be modeled using equilibrium-based (EQ-based) approaches with (constant) height equivalent to theoretical stage (HETS) values, these kinetic effects can limit the applicability of EQ-based LLX models for conceptual design. Non-equilibrium (NEQ) or rate-based modeling can account for detailed mass transfer and fluid dynamics but further increases the nonlinearity and complexity of the respective optimization problems, which should account for closed-loop solvent recovery. To successfully address these complexities, we propose an integrated methodology combining NEQ-based simulation with EQ-based superstructure optimization to design a hybrid extraction-distillation process. An NEQ model is first used to derive operation-dependent HETS correlations, which are then incorporated into an EQ-based superstructure model for techno-economic optimization targeting total annualized cost. This approach balances model fidelity and computational efficiency, providing more reliable solutions by capturing the solvent-specific mass transfer behavior. We illustrate the methodology for a dilute acetone-water system with different solvents.

Keywords: Hybrid Processes, Process Design, Superstructure Optimization

INTRODUCTION

Liquid-liquid extraction (LLX) is a critical technique for separating mixtures that are sensitive to high temperatures, highly diluted, or exhibit azeotropic behavior [1]. The technique relies on the distribution of target components between two immiscible liquid phases, making it particularly effective when conventional distillation alone becomes impractical or even impossible. Despite its usefulness, LLX requires subsequent solvent recovery, which can be accomplished by distillation in many cases. As a result, hybrid extraction-distillation processes have emerged as a standard combination in the chemical and biochemical industries, integrating the strengths of both unit operations and offering potentially lower energy consumption and improved selectivity for challenging separations [2].

Despite its widespread industrial application, the design and optimization of LLX processes remain challenging, mainly due to the necessity of selecting a suitable solvent. In contrast to distillation, where equilibrium-based (EQ-based) models with constant values for the height equivalent to a theoretical stage (HETS) are mostly considered sufficient to yield accurate results, LLX is significantly affected by kinetic phenomena, e.g., fluid dynamics, due to the much lower density difference between the phases compared to vapor-liquid equilibria in distillation, and mass transfer limitations [3]. Therefore, it has been reported that an EQ model with constant stage efficiencies [4] or a constant HETS [5] can introduce considerable inaccuracies when designing LLX processes.

Non-equilibrium (NEQ) models, which incorporate a dedicated description of mass transport and fluid dynamics, offer a superior representation but are associated with a substantial increase in model complexity [3,6], as well as additional requirements of system-specific transport property data and equipment-specific hydrodynamics and mass transfer kinetics. Additionally, the necessary consideration of solvent recovery in a closed-loop process further increases the challenges for an optimization-based design. This complexity represents a significant obstacle to the frequent use of NEQ models in process optimization, particularly in large-scale industrial applications [7].

In a previous study, Kampwerth et al. [3] employed a rate-based NEQ dispersion model of a counter-current LLX column based on population balance equations accounting for complex and interconnected kinetic phenomena. For the considered hybrid process, the rate-based LLX model is complemented by a shortcut model (Fenske-Underwood-Gilliland) for the distillation column for solvent recovery and product purification. By neglecting the mutual solubility of the carrier and the solvent and assuming a sharp split in the solvent recovery column, the process recycle comprises a pure solvent. Therefore, the recycle stream is not explicitly considered, which simplifies the model notably. Based on this model, Kampwerth et al. [3] perform a solvent selection by manually determining the optimal solvent-to-feed ratio based on a sensitivity analysis considering the total annualized costs (TAC) as their objective. Using the Kremser method [8] to estimate the minimum number of EQ stages in the LLX column, Kampwerth et al. [3] determined solvent-specific HETS values based on their optimal process conditions, reporting a broad range for the HETS values ranging from 0.26 m to 1.10 m. In a following study, Kampwerth et al. [6] extend their model by considering mutual solubility of the carrier and the solvent in the two-phase liquid system to include solvent loss in the raffinate and evaluate the impact of different alternatives for raffinate purification. Based on the results of the study, the authors highlight the importance of fluid dynamics and mass transfer phenomena when selecting solvents and designing LLX columns.

In order to expand the scope of the study to an increased solvent search space, Polte et al. [9] combined the developed NEQ model and the design procedure with a computer-aided molecular and process design method (CAMPD) introduced by Scheffczyk et al. [10]. The combination allows for generating new solvent candidates using a genetic algorithm. The NEQ model framework provides the TAC concerning the optimal solvent-to-feed ratio as a fitness function for the genetic algorithm. The approach successfully demonstrates the automatic evaluation and design of solvent candidates based on a rigorous rate-based LLX model with an enlarged solvent design space. However, the hybrid process was still evaluated based on a shortcut representation of the distillation column, assuming a perfect separation of the product and solvent recycle stream. Moreover, besides the solvent selection, all studies consider a single design degree of freedom (DDoF), namely the solvent-to-feed ratio, due to their chosen model types and assumptions.

In contrast to the latter approach that focuses on the detailed modeling of the LLX column, Kruber et al. [11] proposed an EQ-based superstructure model to optimize the closed-loop hybrid extraction-distillation process in the context of solvent screening. The resulting problem is effectively solved as a successively relaxed mixed-integer nonlinear programming (SR-MINLP) problem [12]. The polylithic solution strategy allows for an efficient optimization of multiple operational DDoF, e.g., the solvent-to-feed ratio as well as the reboiler and condenser duty in the distillation column, and structural DDoF, e.g., the column heights and diameters. Nonetheless, the model relies on pre-specified constant HETS values for the LLX and distillation column. The study did consider these fixed for all investigated solvents and operating conditions.

To overcome the limitations of the individual approaches, an integrated approach that combines the NEQ modeling by Kampwerth et al. [3,6] with an EQ-based superstructure optimization for a hybrid extraction-distillation process [11] is presented in this work. The objective is to develop a reliable method for process optimization that captures the essential features of mass transfer and fluid dynamics in the LLX column without the computational burden of full rate-based representation throughout the entire design process. In the initial phase, the NEQ representation of an LLX column is employed to calculate HETS values specific to the selected solvent and contingent on the operational conditions [6]. Based on the generated data, solvent-specific HETS correlations are generated and incorporated into an EQ-based extraction-distillation superstructure model [11], thereby enabling accurate incorporation of mass transport phenomena in combination with a rigorous closed-loop process optimization. The efficacy of the proposed design approach is illustrated through its application to the separation of a diluted acetone-water mixture. The cost-optimal process designs for a range of solvents are evaluated, with a particular focus on the specific HETS values. Furthermore, the results are compared to those derived for constant HETS values across all solvents and operating conditions. Finally, a conclusion and an outlook for future research opportunities are given.

METHODOLOGY

By combining a rigorous superstructure optimization based on the assumption of EQ conditions with a detailed NEQ-based approach to determine solvent-specific

HETS values, the developed methodology partly preserves the accuracy of the rate-based approach while being computationally efficient for superstructure optimization. A schematic depiction of the methodology is shown in Figure 2. First, a database of HETS values for the LLX column is generated based on calculations for each selected solvent using the NEQ-based simulation at different ratios of continuous and dispersed phases. A polynomial regression is performed to generate solvent-specific surrogate models for the HETS values. Subsequently, an economic superstructure optimization is carried out, incorporating the gained correlation for the HETS value. The following subsections briefly explain the main parts of the procedure.

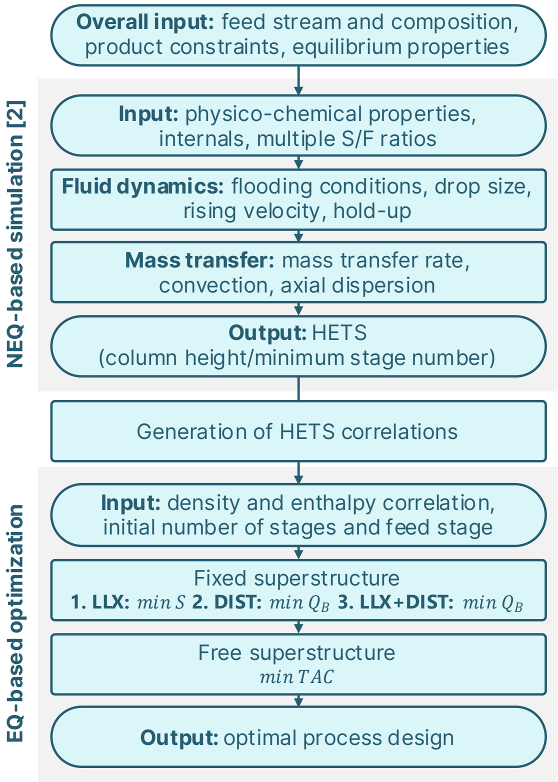

Figure 1. Conceptual framework for integrating HETS correlations derived by NEQ-based simulations into an EQ-based superstructure optimization.

NEQ-based prediction of HETS values

A one-dimensional, rate-based dispersion model is employed to capture mass transfer effects in the extraction column. The primary output of interest is the column height, which reflects the extent of mass transfer required under specified conditions (e.g., temperature, phase ratio, column load). Physical property-based correlations (densities, viscosities, interfacial tension) are used to estimate key fluid dynamic parameters such as drop size distribution, sedimentation velocity, holdup, and dispersion coefficients. These parameters determine interfacial area and residence time available for mass transfer, eventually defining the necessary column height. Once the column height is determined for the required separation and operating condition, the method by Kremser [8] is applied to calculate the minimum number of EQ stages, thus enabling the estimation of HETS. Details on the underlying correlations and boundary conditions regarding the rate-based modeling approach can be found in Kampwerth et al. [3].

To achieve simple HETS-correlations, quadratic, cubic, and quartic polynomial models are investigated based on their corrected Akaike information criterion (AICc) [13]. The AICc enables a comparison of different models by considering the model's accuracy and simplicity, balancing the risks of under- and overfitting. It is generally recommended to use the corrected version of the AIC, which accounts for small sample sizes. Based on the insights gained, a cubic polynomial of the ratio of continuous and dispersed phases results in a sufficiently accurate and simple representation of the solvent-specific HETS values.

EQ-based superstructure optimization

The superstructure model for the hybrid extraction-distillation process is illustrated in Figure 2. The process feed (F) and the lean solvent enter the column at the top and bottom, respectively, to form the countercurrent flow. While the depleted raffinate stream (R) leaves at the bottom, the enriched extract stream (E) is heated to boiling conditions before entering a distillation column. Depending on the mixture topology, the product (P) is either obtained as distillate or bottom product. Prior to the LLX column, the recycle stream is cooled to the operating condition of the extraction and fed to a decanter. The solvent-rich phase leaving the decanter and a solvent make-up stream (S) are recycled to the the LLX column. The solvent-lean phase from the decanter is mixed with the raffinate stream, leaving the process.

The overall structure of the process is predefined, while the height of each unit is introduced as a DDoF by a superstructure formulation with variable feed, reflux, and boil-up positions [11,14]. The superstructure model comprises continuous and discontinuous variables resulting in a mixed-integer nonlinear programming (MINLP) problem, which is efficiently solved as a series of successively penalized MINLP problems [12]. The solution strategy follows a polylithic approach to ensure a robust model and a high-quality local optimal solution based on profound starting values [11]. The second half of Figure 1 captures the core steps of the polylithic solution approach.

The robustness of the model is further increased by using external equations to calculate the equilibrium conditions and the necessary enthalpies. Using external equations notably reduces the number of variables and equations in the process model. Furthermore, dedicated solution strategies can be employed inside the external equations to calculate the different phase equilibria efficiently, further improving robustness and reliability.

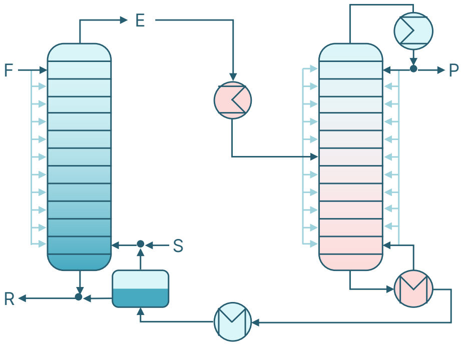

Figure 2. Extraction-distillation superstructure model.

RESULTS

The separation of a diluted acetone-water mixture demonstrates the application of the developed approach. The acetone-water system forms a tangent pinch at high acetone compositions, resulting in high reflux ratios and low energy efficiency for conventional distillation [15]. Previous studies have already suggested the separation by LLX and highlighted the impact of fluid dynamics and mass transport [3,9]. In accordance with these studies, we use the same feed conditions of 76 mol·s^{-1} (5 m^3·h^{-1}) with an acetone content of 2 mol% (5.5 wt%), representing a highly aqueous feed stream. The solvent make-up stream consists of pure solvent. A minimum product purity of 94 mol% acetone and a maximum impurity of 0.01 mol% acetone in the raffinate stream are set as inequality constraints. The necessary physico-chemical property data is taken from the DIPPR database. The non-random two-liquid model (NRTL) represents the EQ behavior, which is fitted to predicted activity coefficients using COSMO-RS [9].

Kampwerth et al. [3] investigated 14 frequently used solvent candidates, out of which five that provide a balanced distribution of the published HETS values are considered in the current study. Therefore, the two solvents with the lowest and highest HETS values are selected, n-butanol (BUT) and methyl isobutyl ketone (MIBK) (low HETS), as well as tetralin (TET) and cyclohexanol (CYC) (high HETS). Toluene (TOL) is also selected as a solvent with an intermediate HETS value close to the reference value of 0.5 m.

The LLX column and the decanter are operated at ambient conditions (25 °C, 1 atm), with a maximum of 15 stages in the LLX column and 50 stages in the distillation column (EQ model). The superstructure models are implemented in GAMS 34.3, and the local SQP solver SNOPT is employed. TAC are determined via the bare module method by Woods [14], using a CEPCI value of 567.5 (2017), a depreciation time of ten years, an interest rate of 6%, and an exchange rate of 0.87 €·$$^{-1}$ [3]. The costs for fresh solvent make-up are initially considered with 1000 €·t^{-1} for all investigated solvents.

Correlation of HETS data

The calculation of solvent-specific HETS values is described in detail by Kampwerth et al. [3]. HETS data are generated for a range of volume ratios using the rate-based simulation model, to fit a cubic polynomial in MATLAB using the built-in "polyfit" function. TOL serves as the benchmark solvent and generally shows an increase in HETS with a rising volume ratio, reflecting changes in solvent flow rate. All solvents follow a similar trend except TET, for which an inversion in phase densities leads to distinct droplet behavior and deviations in the HETS values. The cubic correlations result in a sufficient representation of the data for all five solvents with a minimum R^2 of 0.90 and an average of 0.96.

Superstructure optimization

Figure 3 illustrates the distribution of the capital expenditures (CAPEX) for the optimized flowsheets of all considered solvents for a constant HETS of 0.5 m (left bar) and the correlated HETS (right bar). As expected, TET and CYC exhibit the highest CAPEX, driven primarily by their large HETS values of, on average, 1.2 m and 1.5 m, respectively. The CAPEX of the LLX column for TET and CYC is approximately 50% higher compared to the other solvents. In contrast, TOL shows more moderate CAPEX due to a much lower overall HETS value close to the reference of 0.5 m. Although MIBK and BUT exhibit similar phase diagrams with acetone and water compared to CYC, considering the size of the miscibility gap and the slope of the tie lines, the CAPEX for the LLX column differ strongly.

Interestingly, when comparing the CAPEX based on a constant HETS of 0.5 m, CYC initially appears more cost-effective, but the investment costs increase substantially once volume-ratio-dependent HETS values are incorporated, making it less attractive than MIBK and BUT. Comparing the overall CAPEX, there are differences between the constant and correlated HETS of up to 29%, stressing the importance of considering mass transfer and fluid dynamics, even in a simplified form.

Figure 4 depicts the operating expenditures (OPEX), revealing the dominant influence of solvent make-up flow rates and associated utility requirements. For MIBK, CYC, and BUT, pronounced solvent losses into the raffinate inflate their solvent make-up and drive OPEX substantially above TOL and TET. Losses in the product stream can be tolerated since they account for less than 0.15% of the overall losses for MIBK, CYC, and BUT only.

TET not only shows high investment costs in the extraction column but also suffers elevated utility expenses for distillation due to its large heat of vaporization. As a result, despite differences in the LLX column size and design, the overall TAC across the various solvents primarily depend on the OPEX for the considered economic parameters.

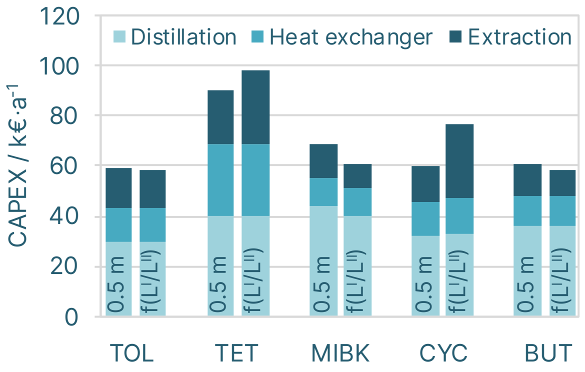

Figure 3. Capital expenditures (CAPEX) of the optimal process design for the solvents toluene (TOL), tetralin (TET), methyl isobutyl ketone (MIBK), cyclohexanol (CYC), and butanol (BUT) with constant and correlated HETS values.

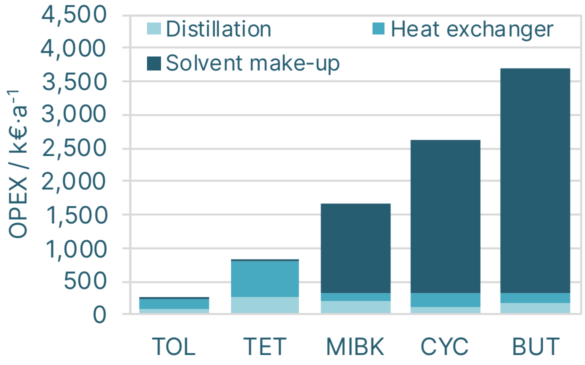

Figure 4. Operational expenditures (OPEX) of the optimized process design for the solvents toluene (TOL), tetralin (TET), methyl isobutyl ketone (MIBK), cyclohexanol (CYC), and butanol (BUT) with correlated HETS values.

The impact of the CAPEX on the TAC is comparably small, especially for those solvents that require large make-up streams, rendering the impact of the fluid-dynamics-related costs negligible. In order to evaluate the impact of the specific solvent costs, the cost for solvent recovery by raffinate treatment are evaluated based on the optimization of a heteroazeotropic distillation (HAD) superstructure model [17] for the solvents MIBK, CYC, and BUT, as these require large make-up streams. Based on the small acetone impurities, the solvent recovery from the raffinate is evaluated as a binary separation problem with a purity constraint of 99.99 mol% of water in the waste stream and a saturated solvent recycle, resulting in an average solvent recovery of 99%. Adjusting the assumed solvent make-up costs on the basis of these calculations, the TAC of the overall process can be reduced by approximately 80% on average. As this model is evaluated separately from the extraction–distillation framework, these corrections should be verified in a closed-loop process model.

In addition to solvent recovery, a straightforward estimation of potential savings through energy integration reveals further cost reduction possibilities. Since the preheater and cooler operate at comparable heat loads for all five solvents, heat integration by means of a heat pump is very attractive. The favorable temperature difference also supports direct integration for a large portion of the heat, saving the investment for a heat pump setup. As illustrated in Figure 5, these measures could yield overall savings of up to 92% of the TAC for the three solvents, making them competitive with TET. Besides improving economic viability, such strategies also shift the balance between capital and operating costs, making the LLX column design a more critical element in the overall process configuration.

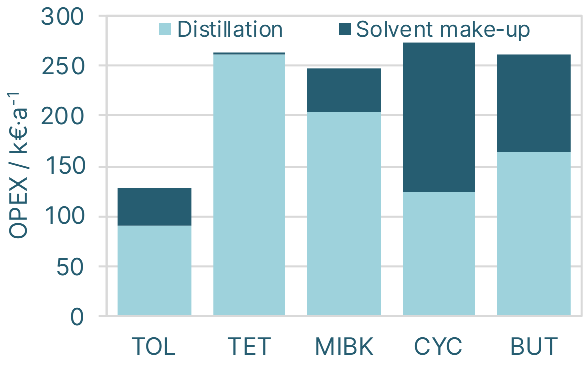

Figure 5. Adjusted operational expenditures (OPEX) with improved solvent recovery for the solvents methyl isobutyl ketone (MIBK), cyclohexanol (CYC), and butanol (BUT) and heat integration for all five solvents.

CONCLUSION AND OUTLOOK

The current work introduces a novel approach that combines NEQ modeling with EQ-based superstructure optimization to design and evaluate LLX processes with integrated solvent recovery. The approach is successfully applied to the separation of a diluted acetone-water mixture, illustrating that solvent-specific HETS are of decisive importance for the accurate design of extraction columns and associated investment costs. If the investment costs are comparably small in respect to the operating costs, as is the case in the current study, solvent recovery including losses in the raffinate, and proper heat integration are decisive for the choice of the best solvent. These results stress the importance of a holistic process design approach, in particular, the consideration of processes with closed recycle streams and heat integration.

Therefore, future research should expand the balance envelope for these processes and investigate a broader range of solvents and separation tasks. Regarding the incorporation of kinetic phenomena, the correlated HETS values should be expanded, e.g., towards a temperature dependency. This opens the opportunity to add the temperature as a DDoF rather than a predefined parameter. However, special care needs to be taken to ensure correct thermodynamic behavior with respect to the liquid-liquid equilibrium. Such extensions will require further refinement of the model formulation as well as improved initialization strategies to account for an increase in process complexity.

REFERENCES

1. Sattler K. Thermische Trennverfahren. Wiley (2012)
2. Blahušiak M, Kiss AA, Babic K, Kersten SR, Bargeman G, Schuur B. Insights into the selection and design of fluid separation processes. Sep Purif Technol 194:301–318 (2008) https://doi.org/10.1016/j.seppur.2017.10.026
3. Kampwerth J, Weber B, Rußkamp J, Kaminski S, Jupke A. Towards a holistic solvent screening: On the importance of fluid dynamics in a rate-based extraction model. Chem Eng Sci 227:115905 (2020) https://doi.org/10.1016/j.ces.2020.115905
4. Sanpui D, Singh MK, Khanna A. Mass transfer studies on ternary systems in a bench-scale liquid-liquid extraction (LLX) column and a comparison with simulations. Korean J Chem Eng 21(2):511–520 (2004) https://doi.org/10.1007/BF02705442
5. Weber B, Meyer C, Jupke A. Performance Map for the Design of Liquid-Liquid Extraction Columns. Chem Ing Tech 91(11):1674–1680 (2019) https://doi.org/10.1002/CITE.201900057
6. Kampwerth J, Roth D, Polte L, Jupke A. Model-based simultaneous solvent screening and column design based on a holistic consideration of extraction and solvent recovery. Ind Eng Chem Res 61(9)3374-3382 (2022) https://doi.org/10.1021/acs.iecr.1c03312
7. Waltermann T, Schlueter S, Benfer R, Knoesche C, Górak A, Skiborowski M. Model Discrimination for Multicomponent Distillation – A Geometrical Approach for Total Reflux. Chem Ing Tech 92(7):890–906 (2020) https://doi.org/10.1002/cite.202000026.
8. Kremser A. Theoretical analysis of absorption process. Natl Petrol News 22:43-49 (1930)
9. Polte L, Raßpe-Lange L, Latz F, Jupke A, Leonhard K. COSMO-CAMPED – Solvent Design for an Extraction Distillation Considering Molecular, Process, Equipment, and Economic Optimization. Chem Ing Tech 95(3):416–426 (2023) https://doi.org/10.1002/cite.202200144
10. Scheffczyk J, Schäfer P, Fleitmann L, Thien J, Redepenning C, Leonhard K, Marquardt W, Bardow A. COSMO-CAMPD: a framework for integrated design of molecules and processes based on COSMO-RS. Mol Syst Des Eng 3(4):645–657 (2018) https://doi.org/10.1039/c7me00125h
11. Kruber KF, Scheffczyk J, Leonhard K, Bardow A. A hierarchical approach for solvent selection based on successive model refinement. Comput Aided Chem Eng 43:325-330 (2018) https://doi.org/10.1016/B978-0-444-64235-6.50060-7
12. Kossack S, Kraemer K, Marquardt W. Efficient Optimization-Based Design of Distillation Columns for Homogenous Azeotropic Mixtures. Ind Eng Chem Res 45(25):8492-8502 (2006) https://doi.org/10.1021/ie060117h
13. Burnham KP, Anderson DR. Model Selection and Multimodel Inference. Springer New York (2004)
14. Scharzec B, Kruber KF, Skiborowski M. Model-based evaluation of a membrane-assisted hybrid extraction-distillation process for energy and cost-efficient purification of diluted aqueous streams. Chem Eng Sci 240:116650 (2021) https://doi.org/10.1016/j.ces.2021.116650
15. Skiborowski M, Kruber KF. Exergy-based optimization for the synthesis of heat pump assisted distillation columns. Comput Aided Chem Eng 53:1351-1356 (2024) https://doi.org/10.1016/B978-0-443-28824-1.50226-X
16. Woods DR. Rules of Thumb in Engineering Practice. Wiley (2007)
17. Kruber KF, Skiborowski M. Topology-Based Initialization for the Optimization-Based Design of Heteroazeotropic Distillation Processes. Processes 10(8):1482 (2022) https://doi.org/10.3390/pr10081482
