Systematic Energy Optimization and Design of Process Alternatives for Separation of Quaternary Azeotropic Mixtures

Jean Pimentel[a*], Péter Mizsey[b]

[a]Budapest University of Technology and Economics, Műegyetem 1, Budapest, Hungary
[b]Advanced Materials and Intelligent Technologies Higher Education and Industrial Cooperation Centre, University of Miskolc, H-3515 Miskolc, Hungary
jppimentell@edu.bme.hu

The separation of homogeneous mixtures is an essential aspect of modern industrial processes that significantly relies on distillation operations. However, distillation has an elevated energy consumption and results in inefficiency in various cases. The non-ideal properties of certain mixtures render their separation unsuitable when employing a single distillation unit, increasing the necessary steps and energy requirements. Because of the relevant role of energy saving in sustainability, a systematic approach must be employed to select the most appropriate separation strategy and identify the operations that minimise energy requirements for product generation. This work employs a systematic approach that utilises residual curve maps to propose viable separation stages and determine the best separation sequence. Various separation strategies are identified via the P-graph framework, which identifies the n-best separation strategies and provides the designer with insightful information concerning the process and its performance. Such a methodology had been previously demonstrated for the separation of ternary mixtures; however, this work constitutes a first step in the development of a systematic approach for the separation of quaternary (or more complex) azeotropic mixtures. The range of separation options, including azeotropic distillation and extractive heterogeneous-azeotropic distillation, are identified by analysing the quaternary residual curves. The potential of this method is demonstrated through a case study involving a mixture of acetone, ethyl acetate, ethanol, and water. The initial set of structures comprises 37 alternative sequences for separation, out of which three interesting alternatives are discussed in detail. The case study demonstrates the potential of the method employed in assessing azeotropic distillation alternatives and facilitating informed decision-making for designers.

1. Introduction

Modern society heavily relies on the chemical industry to satisfy various primary needs. Therefore, the revenues from this manufacturing activity have been steadily growing in the last few decades. Although its growth rate seems to be decreasing, the United Nations (UN) expects that world chemical sales will almost double in quantity by 2030 (UN, 2019). Naturally, the high demand for chemical products results in a high consumption of resources. It has been estimated that about 1,600 Mt of resources were employed in 2015 for the manufacture of chemical products (Levi and Cullen, 2018). The chemical industry accounts for approximately 10 % of the global energy demand (International Energy Agency, 2013). Such intensive consumption rates have raised concern about the depletion of non-renewable resources, motivating research for the reuse and recycling of materials to reduce the requirement for fresh resources (Sheldon et al., 2022).

Regarding this matter, considerable research efforts have addressed the recovery of solvents in the chemical industry. This is primarily driven by the solvents' importance in diverse production processes and the general inefficiencies of their treatment and disposal alternatives. For instance, optimization frameworks have been proposed to find solvent recycling alternatives in the pharmaceutical industry (Chea et al., 2020), where solvents account for 90 % of the process volume and are discarded with relative ease.

To reincorporate them back into the productive chain, the solvent mixture's components must often be recovered with high purity. Distillation is one of the preferred methods for separating liquid mixtures as it can generate high-purity products without adding external components. In simple distillation, the separation is achieved by

exploiting the different boiling points of the mixture's constituents. The process involves bringing together the mixture's vapour and liquid phases in various successive stages within a distillation column. As a result, the more volatile components separate in the vapour phase while the less volatile ones remain in the liquid phase. This enables the recovery of the most volatile constituents at the top of the column and the heaviest ones at the bottom. Nevertheless, various mixtures have non-ideal behaviour that results in the formation of azeotropic mixtures, where the liquid and vapour phase compositions are identical (Richardson et al., 2002). Consequently, azeotropic mixtures cannot be effectively separated using a single distillation tower; instead, distinct strategies must be employed, such as changes in pressure, various distillation columns, liquid-liquid separators, or the inclusion of mass separating agents (MSA).

The conceptual design of these separation strategies entails determining the interconnection of various distillation columns and secondary units, as well as finding the mixing places for the MSA and plausible recycles, i.e., the separation sequence. Consequently, the separation system's design is not a simple task and must be determined systematically to generate the most effective solution accurately. An initial approach for designing plausible separation strategies relies on the analysis of the Residual Curve Maps (RCM), which graphically depict the behaviour of the mixture's thermodynamic equilibria (Dimian et al., 2014). This map provides information concerning the plausible separations and the distillation boundaries. It can be employed to propose plausible separation sequences (Doherty and Caldarola, 1985). Even though the RCM provides the designer with insightful information, the identification of separation sequences is still a daunting task, as numerous separation alternatives and configurations may be found in the same RCM. Consequently, Feng et al. (2000) proposed a framework to identify plausible operations by resorting to discretisation of the RCM. Tao et al. (2003) proposed a methodology to generate separation sequences based on a combination of various feasibility procedures, focusing on the systematic evaluation of recycles. Further optimization-based methods have been proposed for the design of azeotropic distillation columns in homogeneous mixtures, which rely on the combination of shortcut calculations and rigorous models (Kossack et al., 2006). These approaches usually involve the solution of a Mixed Integer Non-Linear Programming problem (MINLP). This problem incorporates binary terms to represent the inclusion or exclusion of units in the separation sequence, along with non-linear models that describe the behaviour of the mixture and operations (Grossmann and Santibanez, 1980). The solution of the MINLP problem renders the best separation sequence according to the criteria considered in the objective function. However, because of the simplifications and uncertainties in the model and the designers' interest in evaluating additional criteria that are not considered in the objective function, the generation of a single separation sequence is often insufficient for decision-making (Voll et al., 2015).

To address this limitation, Feng et al. (2003) integrated their initial unit-identification approach with the graph-theoretic method for process synthesis known as the P-graph framework (Friedler et al., 2022). This framework algorithmically constructs a rigorous superstructure and identifies the n-best solutions to the problem comprised in it. Thus, it can render the best alternative separation sequences. The framework's algorithms exploit the superstructure's properties to enhance the efficiency of the solution process. This is achieved by eliminating infeasible terms, reducing the size of subproblems, and guiding the branching process by resorting to the structure's connectivity. This greatly reduces the computational effort in solving the problem, decreases the complexity associated with binary terms, and permits the determination of the n-best feasible solutions (Friedler et al., 1996). Previous contributions presented a combination of this methodology with rigorous simulation for the automated simulation and optimisation of alternative separation sequences (Pimentel and Friedler, 2021). However, the methods for designing the n-best separation sequences have thus far been applied solely to ternary mixtures. No examination has been presented for complex mixtures featuring multiple components or various types of azeotropes and non-ideal behaviours. This work presents an initial exploration for extending these methods to deal with complex mixtures, e.g., mixtures comprising four or more components. The potential of the method is illustrated with the generation of a set of alternative structures for the separation of a quaternary mixture, including acetone, ethyl acetate, ethanol, and water, which is characteristic of solvent mixtures employed in industrial liquid ink. This initial exploration constitutes a step towards more sustainable decision-making in the separation of complex non-ideal mixtures. The algorithmic generation and evaluation of alternatives considering environmental criteria will help in decreasing energy expenses, reducing general costs, and achieving more sustainable processes.

2. Methodology

Initially, the identification of plausible operating units, such as distillation columns, decanters, and mixers, follows the procedure outlined by Feng et al. (2000). This involves discretising a ternary diagram that represents the mixture's vapor-liquid-liquid equilibrium (VLLE). Herein, the approach is extended to utilise a four-component diagram, providing similar information for the selected quaternary mixture. The non-random two-liquid (NRTL) model is employed to represent the non-idealities of the liquid phase, and the binary interaction parameters

were retrieved from Aspen Plus® database. Subsequently, the generated diagram is discretised by representing its relevant regions via a single material that characterizes the composition of the entire vicinity. For instance, mixtures whose composition lies around the stable and unstable nodes are selected; besides, mixtures close to the distillation boundaries and in the liquid-liquid envelope are also examined. This set of mixtures constitutes the set of plausible materials considered for the design problem and is used to determine the plausible connectivity of the network. At least one discretised region (i.e., material) should exist per distillation region to explore the separation of the entire range of compositions. However, more discrete regions can be utilised depending on the level of detail and accuracy desired by the designer.

The identification of plausible units is performed by defining operations capable of transforming specific materials either into desired products or into intermediate materials that can be further processed to generate the desired components. The set of identified units comprises distillation columns, liquid-liquid separators (decanters), and mixers. Additionally, a combination of these units is also considered to explore the inclusion of extractive-heterogeneous-azeotropic distillation (EHAD) in the separation sequence (Szanyi et al., 2004). This unit involves the integration of a distillation column with a decanter at the top, whose aqueous phase is recycled to the column. Pure water is introduced in the column as MSA.

Simple distillation columns, i.e., columns with a single input and two outputs, are considered. These units are determined by evaluating the mass balance, represented by a straight line in the quaternary diagram, and analysing the direction of the residual curves for each region in the RCM. The decanters, on the other hand, are determined by considering the materials and regions inside the Liquid-Liquid Equilibrium (LLE) envelope. Each material within it is distributed into two phases represented by the materials lying on the LLE boundary. The equilibrium lines indicating the partition of each material inside the envelope constitute a plausible decanter in the synthesis problem. Finally, the set of mixers is defined by considering co-linear materials capable of creating a useful mixture within the process.

The set of units identified and their concomitant materials constitute the basis for designing an effective separation strategy. These units are depicted according to the P-graph representation by separating them into M-type nodes, which depict the materials in the system, and O-type nodes, which represent the operating units in the synthesis problem. Figure 1 illustrates the identification of a distillation unit in a tetrahedron, which separates material F into water and material M1, and its representation as a P-graph.
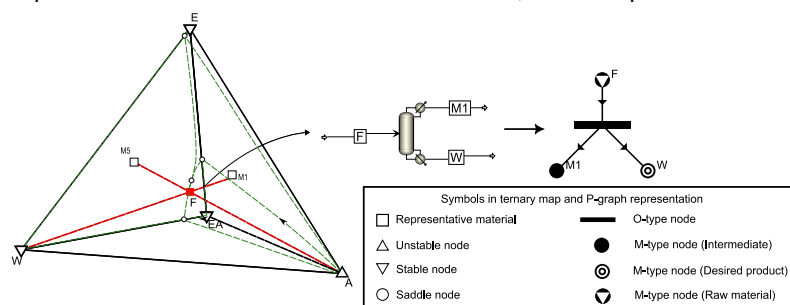

Figure 1: Illustration of units' identification in RCM for the system Acetone (A), Ethanol (E), Ethyl acetate (EA) and Water (W)

The set of operating units and materials are incorporated into the P-graph algorithms. The implementation of the algorithm Maximal Structure Generation (MSG) constructs a rigorous superstructure for the synthesis problem while removing illogical operating units and materials. Then, the algorithm Solution-Structure Generation (SSG) is implemented to generate combinatorially feasible networks, which constitute potential candidates for the mixture's separation, i.e., the separation sequences. Two additional constraints are imposed on the algorithm SSG. First, the algorithm must reject structures that generate by-products, ensuring that the outlet streams exclusively correspond to the set of products defined in the methodology. Second, a limitation is set on the maximum number of units that can produce the same material due to operational considerations. For this initial exploration, the maximum number of units producing the same material is constrained to two.

The initial conditions for the distillation units identified are estimated by resorting to shortcut methods, specifically to the equations of Fenske Underwood and Gilliand (Towler and Sinnott, 2008) implemented via the module DSTWU of Aspen Plus. On the other hand, the initial values of splitting ratios in dividers are initialised by assuming an equal split for all streams, and the decanters were assumed to operate at 1 atm and 298 K. Each combinatorially feasible network is then automatically generated in the simulation environment and optimised via a MATLAB subroutine. This evaluation results in a set of plausible networks for separation. It is important to note that the methodology aims to generate a range of feasible designs for the separation, providing valuable

information regarding the problem and its behaviour during the design step. However, the final selection of the most appropriate structure requires detailed evaluation by the design team.

The initial exploration presented here considers an equimolar feed stream consisting of acetone (A), Ethyl Acetate (EA), Ethanol (E), and Water (W), represented as material F in Figure 1. The optimisation's objective for each structure is to minimise the total heat of the reboilers while ensuring the separation of the mixture into products with a minimum purity as follows: 95 % (A), 90 % (EA), 94 %(E), and 98 % (W). The ActiveX control of Aspen Plus is exploited via MATLAB to automatically construct, simulate, and optimise the selected networks. The optimisation is carried out by resorting to the *patternsearch* function employing the distillate-to-feed ratio, the reflux ratios, and the splitting ratios in dividers as the decision variables. To address convergence issues in the simulator, a penalty function is formulated based on the simulation's final status, rejecting non-convergent points during optimisation, which can be reviewed manually if required.

3. Results

The discretisation of the RCM starts by considering the desired products. Because of the acceptable purities of ethanol and ethyl acetate assumed for the case study, their representative products include materials with higher concentrations of the other constituents. In the specific case of ethanol, the azeotropic mixture of ethanol and water, for instance, is acceptable as a product. This material is termed "E-W", so materials A, EA, E-W, and W are included. Figure 2 shows the materials corresponding to regions adjacent to the distillation boundaries that were considered for the problem. In this case, materials in regions close to the distillation boundary where W is the stable node are represented as M1, those close to the boundary where EA is the stable node are represented as M2, and those close to the boundary where E is the stable node are termed M3. Materials M5 to M12 are determined in an analogous way, but considering the ternary equilibrium formed by EA, E, and W. In this case, material M5 represents the region of the ternary diagram where no LLE exists or where the liquid-liquid partition is not useful to cross the distillation boundary (above the upper LLE partition line shown). On the other hand, material M9 represents the materials inside the LLE envelope whose partition can be used to cross the distillation boundary. The aqueous and organic products of this material's LLE separation are depicted by materials M10 and M11. Materials M6, M8, and M12 symbolise mixtures close to the distillation boundary, and material M7 represents a mixture close to the ternary azeotrope.
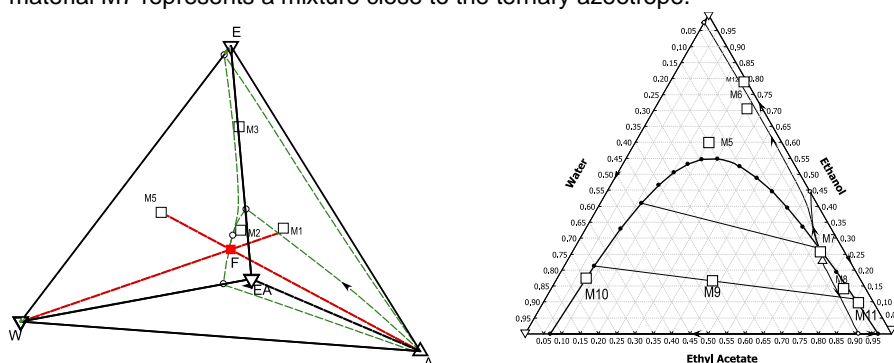

Figure 2: Representation of materials M1 to M12 identified in case study

In this contribution, 13 distillation columns were identified based on the considered materials, similar to those shown in Figure 1. Additionally, 3 decanters and 7 mixers were specified to complement the separation process. The EHAD operation was also included in the structure for the design, which involves a combination of a distillation column and a decanter. This EHAD unit was evaluated as receiving material M5 and freshwater as inputs and generated a mixture of ethanol, water, and EA through the LLE. However, more configurations of this unit could be included for further exploration.

Implementation of algorithm SSG, with the previously mentioned constraints, results in 768 combinatorially feasible solutions. For simplicity, in this initial exploration, only solution structures comprising 4 distillation columns or less are selected for the simulation step. This constraint yields 37 separation sequences that were considered for optimisation in the simulator. Several of these 37 initial structures were deemed infeasible due to mass and energy balance considerations or resulted in repeated solutions. Because of space limitations, only three of the most interesting separation alternatives are shown in Figures 3 to 5. The structures selected fulfil the purity requirements with a tolerance of 0.0005. The total heat of reboilers per unit of feed required for the separation found after the initial optimization is also shown in the figures. The first alternative proposes the indirect distillation of the feed to remove W through the bottom and material M1 through the top. M1 is

subsequently distilled to recover A at the top. The bottoms material is distilled, separating it into E-W and material M7, which is mixed with fresh water to generate material M9. This last material is separated via LLE to generate the EA product and M10, which is distilled to recover additional water. The total reboiler heat required by this separation sequence is 5,068 kJ/kg of feed.
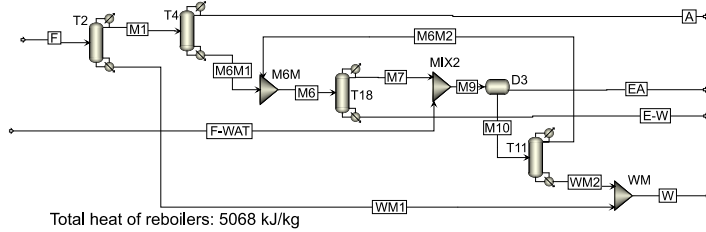

Figure 3: Structure #32 identified by the SSG algorithm as generated in Aspen Plus®

The second alternative of interest is presented in Figure 4, where only three towers are required to perform the separation with the desired purity. There, material A is initially distilled from the feed at the top of the first column. The material at the bottom is mixed with a recycle stream, yielding material M10. The latter is separated to recover W at the bottom of the next column, and the top material is then separated to generate E-W and EA through decanter D3. Although the number of columns in this alternative is lower, the energy required for the separation is significantly higher than in the former option, as the total heat of the reboilers is 6,700 kJ/kg.
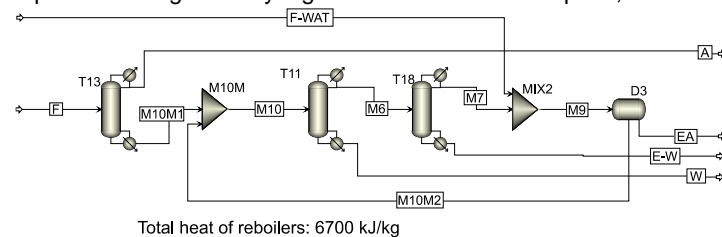

Figure 4: Structure #36 identified by the SSG algorithm as generated in Aspen Plus®

The third structure, depicted in Figure 5, proposes the separation of the feed into material A and material M5. Subsequently, material M5 is separated via EHAD to generate an ethanol-water mixture (EYWY1), with the product EA at the top. The mixture EYWY1 is distilled to generate azeotropic ethanol as the top product and water as the bottom one. The total heat of reboilers in this sequence is 2,406 kJ/kg of feed, resulting in the best alternative found in this initial exploration. The analysis performed suggests superior performance from an energy perspective for the alternative comprising the EHAD.
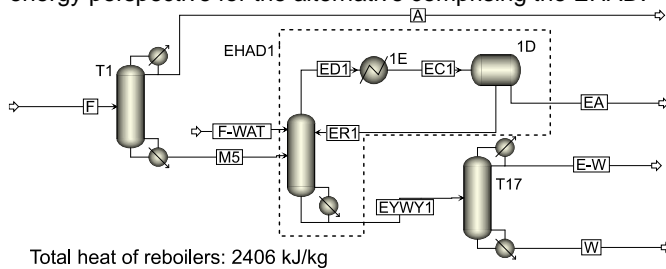

Figure 5: Structure #7 identified by SSG algorithm as generated in Aspen Plus®. The EHAD integrated unit is enclosed by a discontinuous line

Nevertheless, it is essential to highlight that despite conducting the simulation and optimisation using rigorous models, a more in-depth analysis of the generated structures is crucial; specifically, the inclusion of capital expenses and relaxation of the constraints imposed on the SSG is required to generate a well-informed decision about the system. To explore the correct implementation of the alternatives, the sequences could be tested experimentally to verify the adequacy of the thermodynamic models and parameters used in the simulation. The improvement of the initialization of columns by including additional shortcut methods, such as the rectification body method (RBM), may be necessary to develop a fully automated synthesis method, especially to improve the convergence during optimization.

4. Conclusions

This work presents an initial step for extending the systematic generation of separation sequences for azeotropic distillations into mixtures of four or more components. The extension was demonstrated to be plausible by applying it to the case study of a quaternary mixture of solvents, for which a set of alternative separation schemes was successfully identified. This exploration also demonstrated the potential of EHAD for the separation of mixtures when compared to distinct separation sequences. Future work can focus on the implementation of the analysis of capital expenses, the improvement of the optimisation initialisation via additional shortcut methods, and the experimental verification of some of the alternatives generated.

References

Chea J.D., Lehr A.L., Stengel J.P., Savelski M.J., Slater C.S., Yenkie K.M., 2020, Evaluation of Solvent Recovery Options for Economic Feasibility through a Superstructure-Based Optimization Framework. Industrial & Engineering Chemistry Research, 59, 5931–5944.

Dimian A.C., Bildea C.S., Kiss A.A., Kiss A.A. (Eds), 2014, Integrated design and simulation of chemical processes, Computer-Aided Chemical Engineering, 35, Elsevier, Amsterdam, The Netherlands.

Doherty M.F., Caldarola G.A., 1985, Design and synthesis of homogeneous azeotropic distillations. 3. The sequencing of columns for azeotropic and extractive distillations. Industrial & Engineering Chemistry Fundamentals, 24, 474–485.

Feng G., Fan L.T., Friedler F., Seib P.A., 2000, Identifying operating units for the design and synthesis of azeotropic- distillation systems. Industrial & Engineering Chemistry Research, 39, 175–184.

Feng G., Fan L.T., Seib P.A., Bertók B., Kalotai L., Friedler F., 2003, Graph-Theoretic Method for the Algorithmic Synthesis of Azeotropic-Distillation Systems. Industrial & Engineering Chemistry Research, 42, 3602–3611.

Friedler F., Orosz Á., Pimentel Losada J., 2022, P-graphs for Process Systems Engineering. Springer International Publishing, Cham, Switzerland.

Friedler F., Varga J.B., Fehér E., Fan L.T., 1996, Combinatorially Accerelated Branch-and-Bound Method for Solving the MIP Model of Process Network Synthesis, Chapter In: Floudas C.A., Pardalos P.M. (Eds.), Nonconvex Optimization and its Applications, Kluwer Academic Publishers, Norwell, MA, USA, 609–626.

Grossmann I.E., Santibanez J., 1980, Applications of mixed-integer linear programming in process synthesis. Computers & Chemical Engineering, 4, 205–214.

International Energy Agency, 2013, Technology Roadmap Energy and GHG Reductions in the Chemical Industry via Catalytic Processes. <https://iea.blob.core.windows.net/assets/d0f7ff3a-0612-422d-ad7d-a682091cb500/TechnologyRoadmapEnergyandGHGReductionsintheChemicalIndustryviaCatalyticProcesses.pdf>, accessed 04.10.2023.

Kossack S., Kraemer K., Marquardt W., 2006, Efficient Optimization-Based Design of Distillation Columns for Homogenous Azeotropic Mixtures. Industrial & Engineering Chemistry Research, 45, 8492–8502.

Levi P.G., Cullen J.M., 2018, Mapping Global Flows of Chemicals: From Fossil Fuel Feedstocks to Chemical Products. Environmental Science & Technology, 52, 1725–1734.

Pimentel J., Friedler F., 2021, Systematic Design and Evaluation of Energy-Efficient Alternatives of Heterogeneous Azeotropic Distillation: Furfural Case Study. Chemical Engineering Transactions, 88, 619–624.

Richardson J.F., Harker J.H., Backhurst J.R., 2002, Distillation. Chapter In: JF Richardson, JH Harker, JR Backhurst (Eds.), Chemical Engineering, Butterworth-Heinemann, Oxford, UK, 542–655.

Sheldon R.A., Bode M.L., Akakios S.G., 2022, Metrics of green chemistry: Waste minimization. Current Opinion in Green and Sustainable Chemistry, 33, 100569.

Szanyi A., Mizsey P., Fonyo Z., 2004, Novel hybrid separation processes for solvent recovery based on positioning the extractive heterogeneous-azeotropic distillation. Chemical Engineering and Processing: Process Intensification, 43, 327–338.

Tao L., Malone M.F., Doherty M.F., 2003, Synthesis of Azeotropic Distillation Systems with Recycles. Industrial & Engineering Chemistry Research, 42, 1783–1794.

Towler G., Sinnott R., 2008, Chemical Engineering Design: Principles, Practice and Economics of Plant and Process Design. Butterworth-Heinemann, Amsterdam.

United Nations (UN), 2019, Global Chemicals Outlook II: From Legacies to Innovative Solutions. <https://www.unep.org/resources/report/global-chemicals-outlook-ii-legacies-innovative-solutions>, accessed 04.10.2023.

Voll P., Jennings M., Hennen M., Shah N., Bardow A., 2015, The optimum is not enough: A near-optimal solution paradigm for energy systems synthesis. Energy, 82, 446–456.