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Systematic Design and Evaluation of Energy-Efficient Alternatives of Heterogeneous Azeotropic Distillation: Furfural Case Study

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Separation of azeotropic mixtures receives special attention for their impact on various significant industrial processes. Because of the non-ideal behaviour of these mixtures, it is impossible to separate them by conventional distillation. Instead of a single distillation unit, a system of multiple operations is to be employed. Heterogeneous azeotropic distillation (HAD) is an example of this kind of systems, where entrainers are applied to modify the behaviour of the mixture. The selection of the best separation system is a key objective during the synthesis of the process network. However, synthesis of HAD is especially difficult because of the complex interaction between its continuous and discrete features. Therefore, traditional separation network synthesis tools are incapable of solving this problem. In this work, the properties of the ternary vapor-liquid-liquid equilibrium diagram are exploited for systematically identifying plausible operating units that perform the separation of the azeotrope. Subsequently, energy consumption of the entire network is estimated through rigorous simulation. The P-graph framework is employed to represent the system's structure. Additionally, its combinatorial algorithms generate a rigorous superstructure for the synthesis problem, and the set of n-best designs that minimize energy consumption. The method is illustrated by synthesizing the dehydration of furfural through HAD. The results demonstrate that it constitutes a valuable tool for the designer by being effective in the systematic identification and assessment of HAD alternatives.

1. Introduction

Distillation is one of the most widely employed operating units for separation of liquid mixtures. In this operation, the separation is performed thanks to the difference in volatility between the components. More specifically, a stream capable of transferring heat is employed to generate a vapor phase with a high concentration of the volatile constituents, and a liquid phase where remain the less volatile components. Distillation is extensively deployed since products can be recovered with high purity and yield. Nonetheless, the behavior of some materials poses severe non-idealities (Richardson et al., 2002) which render mixtures whose liquid and vapor phase compositions are the same, i.e., azeotropic mixtures. As a result, azeotropic mixtures cannot be separated by a single distillation unit, because a thermodynamic boundary (distillation boundary) prevents further separation.

There are numerous approaches to separate azeotropic mixtures, such as pressure changes and employment of membranes. The most common technique involves the introduction of mass separating agents (MSA) and the use of liquid-liquid equilibrium. The addition of an entrainer alters the thermodynamic behavior of the azeotropic mixture facilitating the separation. This approach benefits from the fact that at certain compositions, some liquid mixtures partitions into two immiscible liquid phases. Therefore, the separation can be performed if the compositions of the immiscible phases rely on different sides of the distillation boundary. This will be referred here as heterogeneous azeotropic distillation (HAD) as it entails the generation of a heterogeneous liquid mixture.

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Any of these approaches require the employment of not only a single distillation column, but of a system of additional operations such as mixers, membranes, and decanters connected as a network. The identification of the operations that comprise this network can be performed by heuristics or by resorting to the analysis of the thermodynamical properties of the mixture, e.g., residual curve map analysis (RCM) (Dimian et al., 2014). Nonetheless, as a result of the numerous alternatives for the elements of the network, it is convenient to employ an algorithmic approach guided by optimization to identify the most suitable separation scheme. The synthesis of such a network entails the formulation of a Mixed Integer Non-Linear Programming problem (MINLP), which is characterized by combining binary terms that represent the existence of the units with the non-linear models that represent the behaviour of the mixture and the operations (Grossmann and Santibanez, 1980).
In order to cope with the difficulties arisen from the combinatorial nature of the problem, this work deploys the graph-theoretical approach based on P-graphs known as the P-graph framework. This framework is capable of generating a rigorous superstructure, besides to enumerating the plausible solutions comprised in it. Moreover, the set of algorithms of the methodology efficiently tackle the difficulties derived from the binary terms, by resorting to the properties of the problem's structure. This methodology has been successfully applied to numerous combinatorial systems, a comprehensive review of some applications related to process network synthesis and supply chain management can be found in the work of Lam et al. (2013), some recent instances are the synthesis of heat exchanger networks (Orosz and Friedler, 2020), the optimization of multiperiodic operations (Bertok and Bartos, 2018) and the analysis of complex socio-technological systems through causality maps (Tan et al., 2021). Regarding the synthesis of HAD systems, Feng et al. (2003) introduced the use of the P-graph methodology for the systematic identification of plausible schemes of separation, however, the feasibility of the final network was determined by means of linear programming. In this work the capability of enumeration of the P-graph algorithm is integrated via ActiveX communication with process simulation, thus permitting the use of complex non-lineal models for the evaluation of the separation alternatives and their subsequent optimization. The method proposed is employed for the identification of plausible networks of HAD applied to the case study of furfural separation.
Furfural – water is an important azeotropic mixture present at the outlet stream of the bioreactor during the industrial production of furfural from lignocellulosic waste (Pulicharla et al., 2016). The furfural has been classified as one of the 30 products derived from biomass with a high potential to compete and replace derivatives from oil. It is precursor of furfuryl alcohol which exhibits similar properties to the ethanol (Werpy and Petersen, 2004). Moreover, it can be used directly as fungicide or as an extractant for refining lubricating oils (Nhien et al., 2016). Consequently, optimization of the separation of furfural has attracted attention during the last years. For instance, Contreras-Zarazúa et al. (2018) evaluated the separation of furfural mixture contemplating systems of thermally coupled distillation. Similarly, Nhien et al. (2016) evaluated alternatives for intensification and heat integration. However, these works have been proposed considering the conventional Quaker Oats process (CQO) as the base case. Herein, the problem is tackled from a process synthesis perspective instead of a process integration and intensification perspective. Consequently, this work deals with the evaluation of the structure for the separation. A methodology is presented for the systematic synthesis of heterogenous azeotropic distillation, based on the previous work (Feng et al., 2003) combined with automated simulation and optimization. The method is illustrated with the generation of a set of alternative structures to the CQO for the separation of furfural-water system. Thus, diversifying the options to be evaluated since the early stages of the process design.

2. Methodology

The P-graph framework relies on a bipartite graphical representation that separates the elements of the network in M-type nodes and O-type nodes. The M-type nodes depict the materials in the system, whereas the O-type node denote the operating units in the synthesis problem. Moreover, the methodology stands on a set of five axioms that allow to discard non-logical structures during the design. These axioms derive in a set of combinatorial algorithms for synthesis and enumeration of process structures. The first of these algorithms is the maximal structure generator (MSG) which constructs a comprehensive superstructure from the initial set of materials and operating units, i.e., a maximal structure (Friedler et al., 1993). The second algorithm is the solution structure generator (SSG). By resorting to this algorithm, it is possible to enumerate the combinatorially feasible solutions comprised in the maximal structure (Friedler et al., 1995).
The determination of plausible operating units, represented accordingly to the P-graph methodology, is carried out considering the procedure described by Feng et al. (2000). To this end the ternary diagram that represents the vapor liquid-liquid equilibrium (VLLE) of the system is constructed by resorting to appropriate thermodynamical models. For details on the construction of ternary diagrams, the reader can refer to the work of Pham and Doherty (Pham and Doherty, 1990). Herein, the NRTL model is employed to represent the non-

idealities of the liquid phase. The binary parameters of the system are retrieved from Aspen Plus® database when available, otherwise they are estimated by UNIFAC method. Once the diagram is generated, it is simplified by linearizing the significant boundaries, i.e., distillation boundary and liquid-liquid envelope (LLE); besides, it is discretized by representing each relevant region with a single material whose composition characterizes the entire vicinity. These materials comprise the set of M-type nodes identified for P-graph methodology.
Subsequently, the set of plausible units for the separation should be determined. Herein, the set of units identified can be partitioned in three groups: distillations columns, liquid-liquid separators (decanters) and mixers. First, the plausible distillation columns are determined by evaluating the mass balance (represented by a straight line in the ternary diagram) and the direction of the residual curves for each region in the RCM. Thus, these operations are identified by specifying the feed, top and bottom materials. Then, the decanters are determined by considering the materials and regions inside the LLE. Each material inside the envelope is distributed in two phases, i.e., organic and aqueous. These phases are represented by the materials that lie on the boundary of the LLE. Consequently, the partition of each material inside the envelope constitutes a plausible decanter in the synthesis problem. Finally, the set of mixers is defined considering co-linear materials that can result in a useful mixture inside the process.
Afterwards, the set of operating units and materials are individually introduced into the P-graph algorithms. The implementation of algorithm MSG generates the rigorous superstructure of the synthesis problem and eliminates illogical operating units and materials. Subsequently, the SSG algorithm is implemented to generate the combinatorially feasible networks, that are candidates for the separation of the mixtures. In this work, two additional constrains are set for the deployment of the SSG algorithm. Firstly, the algorithm must reject structures where by-products are generated, this means that the only existing outlet streams from the process correspond uniquely to the set of products defined in the methodology. Secondly, because of operational reasons, the maximum number of operations that can generate the same material is constrained. In the first stage of the work, this restriction was fixed on one and then it was fixed on two.
Then, the initial conditions for the distillation units included in the maximal structure are estimated by resorting to shortcut methods. Subsequently, each combinatorially feasible structure is simulated and optimized, thus rendering the set of plausible networks for separation. It is worth noting that the methodology intends to generate a set of feasible designs for HAD, which constitutes a valuable tool for the design step as they provide useful information regarding the problem and its behavior. However, the selection of the more appropriate structure requires detailed evaluation from the design team. Figure 1 summarizes the methodology proposed and employed in the present work.

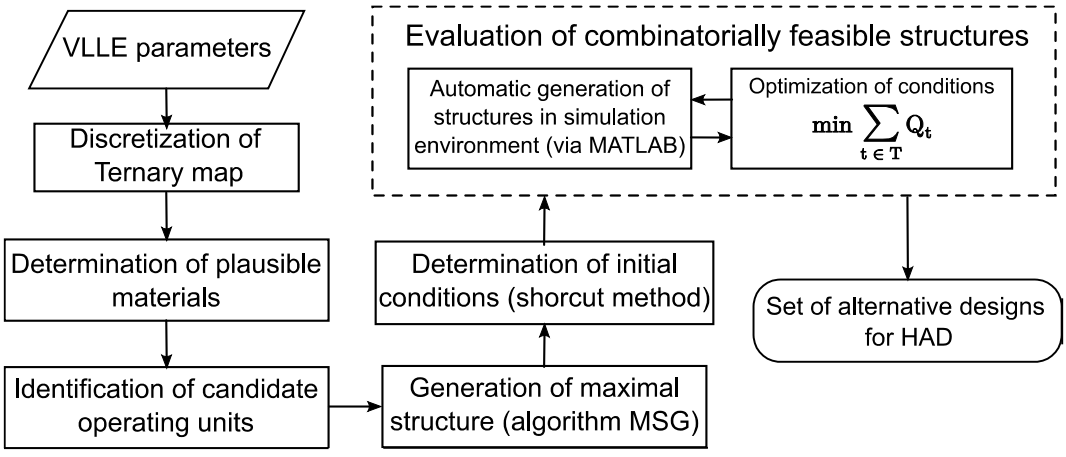

Figure 1: Methodology for generation of a set of alternative systems for HAD

In this work, an algorithm was designed and programmed in Matlab® to automatically introduce and evaluate the structures in Aspen Plus®V10. The feed stream considered is composed by 5.6 % furfural, 91 % water and 3.4% of methanol, similarly to the outlet of the reactor during production of furfural (Zeitsch, 2000). The initial optimization of each structure aims at minimizing the total heat of the reboilers, searching for the feasible conditions that separate the mixture in products with a purity larger than 99 % (w/w). The products considered are the individual constituents of the feed mixture. To this end, the functions *patternsearch* and *fmincon* are implemented in Matlab® considering the distillate to feed ratio and the reflux ratio as the decision variables. The parameters needed for initialization of the distillation units were estimated resorting to the shortcut method of

Fenske-Underwood-Gilliand (Towler and Sinnott, 2008). Moreover, equal separation ratio was assumed for the outlets of splitters which operate with no pressure drop, besides the decanters were considered to operate adiabatically. Additionally, to circumvent issues related to the convergence of simulator, a penalty function was formulated depending on the final status of the simulation, thus rejecting non convergent points during optimization.

3. Results

The resulting ternary diagram is illustrated in Figure 2a. and its subsequent simplification is depicted in Figure 2b. The discretization is based on the work of Feng et al. (2000) in which the relevant regions of the diagram are represented by different materials. In this work, the discretization started by considering the adjacent regions to the distillation boundary; 12 materials were selected to represent both sides of this line (M1,1-M1,6 and M2,1-M2,6). The regions that are not close to the distillation boundary and are out of the LLE were termed as M3 and M4; additionally, some regions (M4-1 and M4-2) were included to increase the accuracy of mixtures close to the feed. Moreover, inside the LLE, four equilibrium lines were employed to subdivide this region into four sections, each represented by regions M5 to M8. Organic phases of each of these subsections are depicted by subindices 1, whereas subindices 2 stand for the aqueous fractions. Furthermore, plausible binary mixtures were considered by including 8 regions on the edges of the ternary diagram and products are considered as separate regions. As result of this discretization, 40 materials were determined to represent the problem together with the feed stream. These materials are also depicted in Figure 2b by means of circles. Moreover 55 distillation units were proposed to be introduced in P-graph methodology. Figure 2b. shows an example of identification for the specific case of the direct distillation of the feed. Additionally, 10 decanter and 28 mixers were specified.

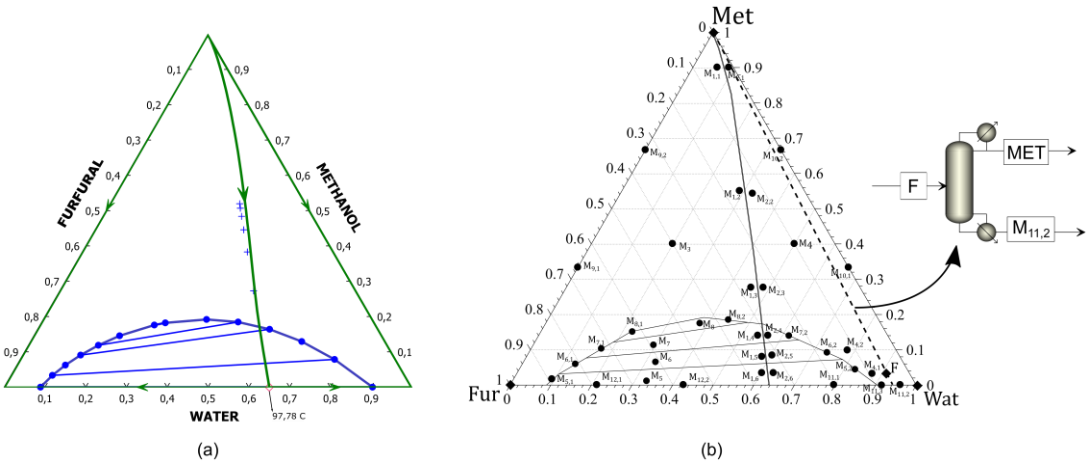

Figure 2: Ternary diagram for the system Water-Furfural-Methanol. a) generated by NRTL model, b) simplified and discretized version

Implementation of algorithm SSG with the constraint of at most one operation generating each material rendered 76 plausible structures. On the other hand, when this limit was increased to two operations, more than 2 million structures were enumerated. Various of the 76 initial structures were found to be infeasible in the light of the mass and energy balance. To illustrate the capability of the methodology for designing different structures, three selected networks are depicted in Figures 3 to 5. Additionally, each figure indicates the total heat of reboilers per unit of feed required for the separation after initial optimization under the given conditions.

In CQO process the feed is initially mixed with one of the outlet streams from the decanter. This mixture is subsequently distilled to obtain water in the bottom of the column (Contreras-Zarazúa et al., 2018). As it can be seen in Figure 3, the network found by the methodology proposes the mixing of the feed stream with the top product of the distillation column that generates furfural, and the bottom of the one that generates methanol. This mixture is subsequently introduced into a decanter unit. In this case, the first pure material obtained is water similarly to the CQO process, nonetheless, the feed is introduced into a decanter before undergoing any distillation.

In the second alternative (illustrated in Figure 4) the feed stream is mixed with the aqueous phase of the decanter, and the mixture is distilled to recover methanol in the first place instead of the water as in the conventional process. The third structure depicted in Figure 5, proposes the separation of the feed stream in

two materials, one of them is introduced in a distillation column, while the other is mixed and introduced into a decanter. Regarding the heat of reboiler necessary for these separations, the lowest value after the initial optimization was obtained by the structure number 9, illustrated in Figure 4. However, it is worth noting that even when the simulation and optimization were performed with rigorous models, it is important to perform a more profound analysis of the structures generated. Separations by HAD are characterized for being sensitive systems, whose simulation is strongly affected by numerous factors such as changes in the initial conditions, besides, the nonlinearity of the system which can derive in multiple steady states for the simulation (Dimian et al., 2014).

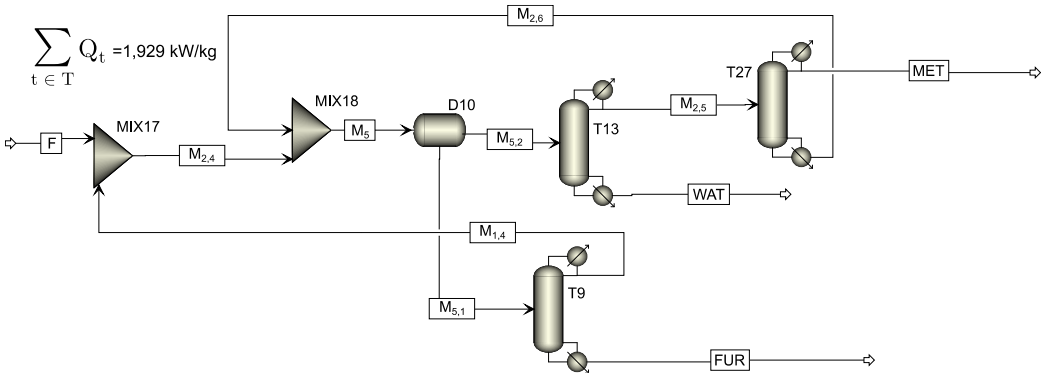

Figure 3: Structure #40 identified by SSG algorithm, simulated and evaluated in Aspen Plus®.

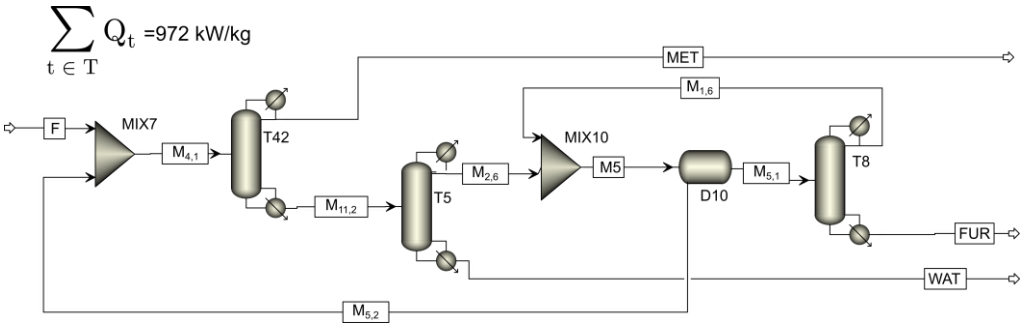

Figure 4: Structure #9 identified by SSG algorithm, simulated and evaluated in Aspen Plus®.

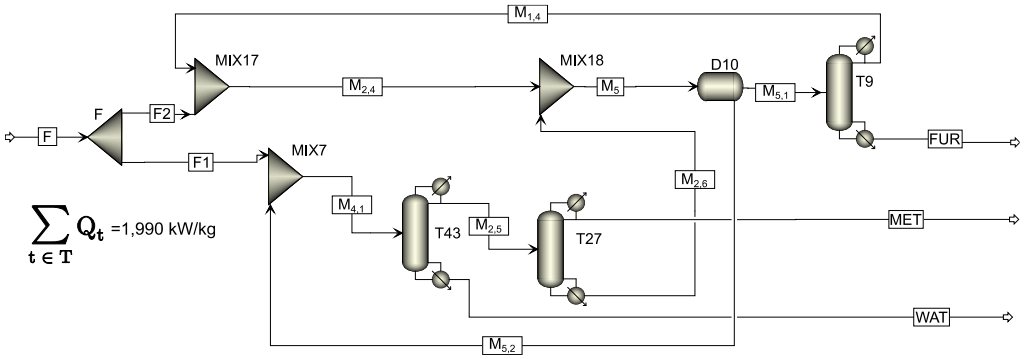

Figure 5: Structure #43 identified by SSG algorithm, simulated and evaluated in Aspen Plus®.

4. Conclusions

This work presents a methodology for the systematic generation of plausible networks for the separation of azeotropic distillations. For this, an algorithm was designed to introduce and evaluate the combinatorially

feasible structures rendered by the P-graph framework in a commercially available simulation software. The methodology was demonstrated by applying it to the case study of furfural separation. The methodology provides a comprehensive set of structures that gives to the designer various alternatives for the selection of the final design. The final decision can be supported by the consideration of alternative indicators such as operability, flexibility, or sustainability. Future work can focus on the implementation of the third algorithm of the P-Graph methodology, i.e., accelerated branch and bound algorithm (ABB) to decrease the search space of the combinatorially feasible structures.

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