Rigorous Separation Design. 1. Multicomponent Mixtures, Nonideal Mixtures, and Prefractionating Column Networks

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Currently, there is a lack of reliable computational methods to automatically synthesize separation networks within specific product targets. Computational methods exploring the combinatorial wealth of different separation configurations, while simultaneously selecting feasible or detecting globally optimal operating conditions, are not available for problems of practical size. In this paper, we extend the minimal bubble point distance algorithm embedded in the temperature collocation methodology to rigorously design complex networks to separate nonideal multicomponent mixtures into products of desired purity using heat-integrated prefractionating columns. Our employed inverse design procedure enables the systematic design of physically realizable separations for mixtures with a large number of species. The computer procedure robustly converges to the desired purity targets, unless the desired purity target is thermodynamically impossible to realize. The algorithm also rapidly identifies infeasible specifications without fail. Finally, synthesized networks were validated with AspenPlus matching exactly the inverse design results with the target purity. The rigorous flowsheet design combined with validation of the networks with commercial flowsheet simulators enables the systematic design of energy-efficient separation networks. The methodology is ready to address currently unresolved design problems such as the computer-aided design of energy-efficient separations, the design of biorefineries, or new process designs for carbon sequestration.

1. Introduction

The increasing demand on energy efficiency and environmental sustainability of chemical manufacturing renews the interest in systematic process design with ecological or energy targets.1,2 Distillation is arguably the most significant chemical unit operation in industrial practice, responsible for about 3% of total U.S. energy consumption.3 Accordingly, even a small improvement in the distillative separations would yield huge energy savings. To harness possible energy improvements, the use of thermodynamically integrated complex columns has been suggested.4–12 For example, thermally coupled distillation columns known as Petlyuk configurations have only require one reboiler and one condenser, independent of the number of components to be separated. Wright13 proposed the divided wall column, in which the prefractionator is transferred inside the second tower so that the entire configuration can be realized in a simple unit. Both structures are typically more energy efficient than conventional simple columns. Recent work by Luyben’s group15 shows practical and effective control strategies for heat integrated columns including divided wall columns. Although the final verdict is still out, it appears that controllability of complex heat-integrated columns is not a problem, if methods such as Luyben’s are applied with care.

Therefore, current research aims at novel methods for discovering energy-efficient configurations systematically. Until recently, however, there were no rigorous algorithms to synthesize complete separation flowsheets without limiting assumptions of the thermodynamic vapor—liquid equilibrium model or restrictions in its applicability like sharp splits or non-distributing species. Purely combinatorial superstructure approaches have been pioneered by the mathematical programming community.3,16–17 Recently, structural approaches specifically addressing synthesizing complex network structures have led to the possibility of engineering all possible configurations systematically.18 However, to judge whether a certain configuration can actually achieve the desired purity, a detailed design including realizable column profiles is needed.

Flowsheet synthesis poses two main problems. The first design stage asks for configuration and operating conditions of a simple column such that a known feed or multiple feed streams can be separated into a set of product streams with desired compositions. Columns with only one feed—a distillate and bottom products—are generally known as simple columns. Columns with more than one feed or more than two products are termed complex columns. The configuration parameters for a column, simple or complex, include the number of stages in each section as well as the location of the feed tray and the number and composition of the product cuts. The operational parameters include the reflux and reboil ratios which are linked by energy balances. For synthesizing entire networks, the product purities must not only satisfy final product purity targets but, more challenging, each intermediate product must reach such compositions so that the subsequent step or multiple steps are also thermodynamically possible. Especially in complex networks, these intermediate cuts do not always fall into the sharp split category, a requirement often demanded by existing design methods.

The second design stage seeks for the specifications of the entire network. Classical separation design aimed at sequencing series of simple columns each equipped with a condenser and reboiler.19 Recent research and modern practice such as crude refinery trains suggest that simple energy networks are seldom energy optimal. However, a complex heat-integrated network is overall feasible, only when each of its steps and therefore each and every column section in the network are thermodynamically feasible. Thus, separation design requires a multiple step design strategy in which a single operation—simple or complex—may make sense only when completing the entire network. Again, the individual columns of the Petlyuk config-

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uration render a meaningful and energy efficient flowsheet as an ensemble; the prefractionator could never be found by classical sequential (step-by-step) reasoning. Accordingly, the second design stage requires a creative search for structural alternatives. Also, for an entire network to satisfy minimum energy demands, a single column should not be optimized locally without considering the entire separation train. For example, the Petlyuk column prefractionator produces only a sloppy split; the entire configuration with thermal coupling produces pure products with reduced energy consumption compared to a sequence of simple columns.

To avoid computational intractability, we have for the moment incorporated specific flowsheets as generated by Agrawal’s method. This step can be automated as described by Agrawal but has been omitted here to focus on ensuring rigorous profiles. We have successfully implemented orthogonal collocation on finite elements (OCFE). For complex separation network design, this approach substantially reduces the problem size without a significant loss in accuracy compared to the rigorous tray-by-tray computations. Although collocation has been used previously in separation design,29–31 this paper demonstrates the temperature collocation29 with a minimum bubble point distance (BPD)30,31 criterion for the rigorous design of entire flowsheets to separate nonideal mixtures, multicomponent mixtures, including prefractionating and complex column configurations. Finally, among all feasible separation networks, we typically are interested in identifying the solution that minimizes a user-defined cost objective. Recently, energy cost and emission reduction have gained significance in the search for new separation solutions.

The paper is organized as follows: First, a methodology section addresses both the structural as well as the parametric challenges of the process design problem. Results and applications demonstrate a rigorous design to separate a quaternary nonideal mixture into almost pure products. A column design to separate a 10-component mixture with three different product distributions is addressed in section 3. Furthermore, the design of prefractionating complex column networks to separate a quaternary mixture of alkanes is described. To demonstrate that the proposed designs are realistic and industrially realizable, equivalent network configurations are validated with rigorous tray-by-tray Aspen Plus simulation in section 4. Finally, sections 5 and 6 offer a discussion and conclusions.

2. Methodology

2.1. Inverse Design Procedure. Despite the common misconception of distillation as a mature field, complex column configurations for enhanced energy efficiency and extractive or reactive separations are an open field of research.32–35 In general, the design of distillation columns can be performed by forward performance simulation. The classical design simulation computes product purities based on a given feed and column design specifications (e.g., total column tray, feed tray, reflux ratio, etc.). This approach requires trial-and-error adjustments of operating conditions and cannot guarantee desired product purities, because they are results of the forward computation not input design specifications. Specifying product purities before searching for feasible column configurations leads to an inverse design method. Thus, inverse design seeks optimal column dimensions and operating conditions for desired product purities. Inverse separation network design to achieve desired product quality specifications requires a rigorous convergence criterion, so that the network can be built in practice. Our group advocates the precise intersection of liquid composition profiles for any pair of equivalent rectifying and stripping sections as a rigorous criterion to ensure thermodynamic feasibility and practical realizability of a separation column. This criterion has been formulated mathematically as the minimum bubble point distance criterion in previous work.29 In addition, a rigorous inverse design methodology for complex column networks has to meet the following requirements: (i) the search for configurations should incorporate all thermodynamically admissible combinations of simple and complex column equipment to achieve any type of product distribution such as in prefractionating, sharp, nonsharp, and sloppy splits; (ii) liquid composition profile equations should admit all phase equilibrium relationships for ideal, nonideal, as well as azeotropic mixtures; and (iii) column profiles must exactly intersect in feasible designs, while infeasible design specifications are characterized by a gap in at least one pair of composition profiles in adjacent column sections. Thermodynamically impossible specifications lead to nonzero bubble point distances. These requirements have been incorporated in an inverse design methodology known as temperature collocation with rigorous computation of the minimum bubble point distance (BPD). The methodology has two main elements briefly reviewed in the next subsections: (1) rigorous liquid composition profile computations and (2) a bubble point distance criterion for network feasibility. More details can be found elsewhere.29

2.2. Rigorous Profile Computation. Our method departs from the generalized column profile equations proposed by Hildebrand and co-workers36 based on early work by Doherty and co-workers.37 Equation 1 introduces two new design quantities, the generalized reflux, $R_\Lambda$, and the difference point composition, $X_{\Lambda y}$. The difference point composition, $X_{\Lambda y}$, is equal to the distillate or bottom composition in conventional rectifying or stripping sections. In complex column sections, such as the intermediate section of the Petlyuk configuration, it can be interpreted as the concentration difference between the vapor and liquid stream exiting the section. In this sense, $X_{\Lambda y}$ expresses the operating line conditions in a similar fashion to that of the product purity in simple column sections. The net flow of each section, $\Delta$, is equal to the difference between vapor and liquid flow rates, $\Delta = V - L$. Positive net flow means an upward stream corresponding to an equivalent rectifying section. Negative net flow signifies a downward stream as it occurs in equivalent stripping sections. Accordingly, intermediate sections can be categorized into equivalent rectifying sections, in which net flow is upward, and equivalent stripping sections, with a net downward flow. The generalized reflux, $R_\Lambda$, is the recirculation ratio belonging to a column section with the same conceptual function as the reflux in conventional columns.

$$\frac{dx}{dn} = \left(1 + \frac{1}{R_{\Lambda x}}\right)(x_y - y_y) + \frac{1}{R_{\Lambda}}(X_{\Lambda y} - x_x)$$

with $R_{\Lambda} = L/\Delta, X_{\Lambda y} = (Y_{\Lambda y} - Lx_x)/\Delta$  

(1)

Where, $x_x$ and $y_y$ are the liquid and vapor compositions in the phase equilibrium relationship, and $x_x$ and $y_y$ are the liquid and vapor compositions of the streams entering a column section.

Temperature collocation transforms the generalized column profile equations in eq 1 into continuous composition profiles with the bubble point temperature, $T$, as a new independent integration variable, as shown in eq 2. This temperature, $T$, is equal to the tray temperature at each stage but also corresponds to its bubble point, since vapor and liquid streams are in phase equilibrium. Fortunately, the difference point equations also describe the liquid composition of simple column sections, thus
rendering a single mathematical expression for all sections in any separation network, whether they are complex or simple.

\[
\frac{dx_j}{dt} = \left( \frac{1}{R_A} (x_j - y_j) + \frac{1}{R_s} (x_N - x_j) \right) \times \left( \sum_{j=1}^{n} \left( \frac{1}{R_A} (x_j - y_j) + \frac{1}{R_s} (x_N - x_j) \right) K_j \right)
\]

The profile equations in eq 2 are solved for each species composition, \(x_j\), by global collocation of orthogonal polynomials on finite elements with temperature as independent variable. A detailed derivation of the temperature transformation is given elsewhere. \(^{29}\)

The procedure to compute the composition profiles of all columns in a network based on solving eq 2 for each column section is displayed in Table 1 and Figure 1. For each column, the first step consists in specifying the product purities, and for a simple or complex column in terms of molar composition, \(x_{AP}\), or fraction recovery, \(F_{RP}\), and design parameters such as reflux ratio. Step 2 calculates all product flow rates by global mass balances in each column of the network; this step is a linear algebraic problem. Step 3 involves the computation of the stationary nodes in each column section by the implementation of consecutive mass balances in each section and bubble point temperature calculation; these stationary nodes are defined by the values of \(x_{AP}\), \(y_{AP}\), \(T_{AX}\), \(L\), and \(V\). The calculation of the column profile parameters, \(R_s\), \(X_{AP}\), and \(\Delta\), is given in steps 6 and 7, and the stable pinch point of each section, \(T_{pinch}\), is computed in step 5 to be used in the next two actions. Steps 6 and 7 inspect a shortcut feasibility test based on the existence of an attainable temperature window, \(^{28}\) between any pair of equivalent rectifying and stripping column sections. If specifications pass the shortcut feasibility test, steps 8 to 14 are executed to compute all liquid composition profiles of all species in each section by solving eq 2 between the stationary node, \(x_{AP}\), and stable pinch, \(T_{pinch}\), using orthogonal collocation on a finite element in each column section. The detail information about orthogonal collocation on finite elements can be found in a previous publication. \(^{29}\)

For regular rectifying sections, the generalized reflux becomes the classical reflux ratio, and the difference point is equal to the distillate composition. In equivalent rectifying sections, the difference point equation does not correspond to a product leaving the section. Yet, the component balances for an equivalent rectifying section closes the component balances with the difference point in the same way the distillate determines the operating line equations. For the computation of a complex column section, we choose an intermediate product, whose composition constitutes a starting point of the composition profiles. Accordingly, the composition profiles described by eq 2 for any two complex column sections emerge from the respective intermediate product node. Similar considerations apply to equivalent stripping sections.

### 2.3. Bubble Point Distance and Global Feasibility Test

After computing the liquid composition profiles of all column sections, the minimum \(BPD\) is defined as the globally minimum distance between each pair of adjacent column sections. In each section, the continuous temperature column profile equations are a set of polynomial functions for each composition in terms of the bubble point temperature as an independent variable. Since all composition profiles, \(x_j(T)\), are approximated by polynomial functions, the minimum BPD is found easily using polynomial arithmetic. A complex column is feasible, if and only if the sum of all minimum profile distances of any pair of equivalent rectifying, \(r\), and stripping, \(s\), column sections is within a small tolerance of zero, as in expression 3, in which the sum of all its column section bubble point distances is still a scalar. An entire separation network is feasible, if and only if all its simple or complex columns, \(k\), are feasible. The network feasibility is given in expression 4.

\[
\psi(k) = \sum_{i=1}^{K} \min \text{ BPD}(T) < \epsilon_1
\]

\[
\Psi(k) = \sum_{i=1}^{K} \psi(k) < \epsilon_2
\]