A novel framework for simultaneous separation process and product design

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Abstract

The objective of this paper is to introduce a systematic framework for simultaneous solution of process/product design problems related to separation. This framework is based on the recently developed property clustering approach that allows one to perform design calculations on a component-free (or composition-free) basis. Removing the composition dependency from the design problem enables the simultaneous consideration of process and product selection and optimization. The clustering concept is based on the observation that properties, unlike mass, are not conserved and consequently they cannot be tracked among process units without performing component material balances. To overcome these limitations the use of property-based clusters has been proposed. The model derivations and reformulations to cluster-based models are presented and the usage highlighted through a simple proof of concept example and a case study.

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1. Introduction

Aside from reaction systems, the primary task of most processing units is to tailor properties of various streams throughout the process. Furthermore, the use of streams and species throughout the process is primarily driven by the need to satisfy certain properties in the processing units. Notwithstanding the critical role of properties in designing a process, the conventional approach to process design is based on tracking mass and energy throughout the process. Properties are considered indirectly by selecting species as well as operating conditions and ensuring that the resulting properties are acceptable. This approach is quite limiting since the insights associated with properties are masked by species and operating conditions. Alternatively, properties should be tracked and integrated explicitly. The framework for property integration has been presented recently [1–3] and is based on existing property clustering techniques [4]. It is a holistic approach to the tracking, manipulation, and allocation of properties throughout the process. The application range of the original clustering approach is extended by deriving cluster based unit operation models. The models are derived from the fundamental process models and reformulated with respect to clusters. The objective being to replace component based material balances with cluster-based material balances without any simplification or loss of information. Another advantage of the clustering concept is that, by removing the compositions as variables, even a large dimension problem solution can be visualized in the two- or three-dimensional space.

Design of compounds with specified properties is a typical example of product/process design problems, where the clusters together with their target properties are first determined and then molecules (and/or mixtures) that satisfy the targets are determined. In this integrated problem, the process target values are used to generate product data while the product target values are used to generate the process data. The scope of this approach is potentially very large—from simultaneous design and selection of heat exchangers and process fluids to mass exchangers and solvents/agents. This methodology may be employed to design novel separation schemes involving distillation and adsorption processes by removing the composition dependency from the problem, thus yielding the property targets for the components to
be separated. Once the property targets have been identified, the corresponding components may be identified using molecular design techniques.

2. Process and product design issues

Traditionally process design and molecular design have been treated as two separate problems, with little or no feedback between the two approaches. Each problem has been conveniently isolated or decoupled from the other. Fig. 1 shows a schematic representation of the two problems, e.g. the required inputs and solution objectives of the different design algorithms. Both approaches have some inherent limitations due to the amount of information that is required prior to invoking the design algorithm. When considering conventional process design methodologies, the selected species are chosen from among a list of pre-defined candidate components, therefore, limiting performance to the listed components. On the other hand, with molecular design techniques, the desired target properties are required input to the solution algorithm. Once again these decisions are made ahead of design and are usually based on qualitative process knowledge and/or experience and thus possibly yield a sub-optimal design.

To overcome the limitations encompassed by decoupling the process and molecular design problems, a simultaneous approach as outlined in Fig. 2 is proposed. Using this approach the necessary input to the methodology is the molecular building blocks and the desired process performance, for the molecular and process design algorithms, respectively. The final outputs of the algorithm are the design variables, which facilitate the desired process performance target and the molecules that satisfy the property targets identified by solution of the process design problem. The strength of this approach is to identify the property values that correspond to the optimum process performance without committing to any components at this stage. This is a critical characteristic for property integration. These property values are then used for the molecular design, which returns the corresponding components. One inherent problem with this approach is the need to solve the process design problem in terms of properties and not components. The conventional decoupled solution methodology presented in Fig. 1 can be described as a “forward” problem formulation, whereas the simultaneous solution approach given in Fig. 2 consists of solving two “reverse” problems. Solving the process design problem in terms of properties corresponding to the desired process performance identifies the design targets. In principle this part is the reverse of a simulation problem. Similarly solution of the molecular design problem to identify candidates that match the optimal design targets is the reverse of a property prediction problem. Thus, the design targets are described by constitutive variables like physical properties and/or phenomena, such as reaction rates, equilibrium constants and mass/energy transfer rates. The constitutive variables are related to the process (intensive) variables such as temperature, pressure and composition through a constitutive model.

3. General problem formulation

A general process/product synthesis and/or design problem can be represented in generic terms by the following set of equations:

\[
F_{\text{Obj}} = \min \left\{ A^T y + f(x) \right\}
\]

\[
h_1(x, y) = 0
\]

\[
h_2(x, y) = 0
\]
4. Reverse problem formulation

In principle, the process model equations consist of balance equations, constraint equations and constitutive equations [5]. The model type and complexity is implicitly related to the constitutive equations, hence decoupling the constitutive equations from the balance and constraint equations will in many cases remove the model complexity. This provides the foundation for two reverse problem formulations:

1. Given input stream(s) variables, equipment parameters and known output stream(s) variables, determine the constitutive variables.
2. Given values of the constitutive variables, determine the unknown intensive variables (from the set of temperature, pressure and composition) and/or compound identity and/or molecular structure.

As long as the targets are matched, the process model equations (minus the constitutive equations) do not need to be solved again. It should be emphasized that optimization problems based on reverse simulation problems, are not limited by the application range or complexity of the constitutive equations. Therefore, the solution is easy and can be visualized. Another advantage is that for the second reverse problem, any number of independent models may be used, as long as they match the target constitutive variable values. This implies that more than one process and/or product can
be identified by matching the design targets, thus it is possible to determine all feasible solutions. Once the feasible solutions have been identified, the optimal solution may be found by ranking the solutions according to a performance index.

4.1. Illustrative example of reverse problem formulations

A simple, yet illustrative example of the application of reverse problem formulations is the solution of a solvent-based mass exchange problem. Consider a wastewater stream with a flowrate of \( F_w \) and a molefraction of phenol of \( X_1 \). Due to environmental regulations the phenol content must be reduced to a molefraction of \( X_2 \). Using the reverse problem formulation methodology, solution of the balance equation provides the necessary maximum solubility \( S \):

\[
S = \frac{(X_1 - X_2)}{F_w} \tag{7}
\]

where \( F_w \) is the solvent flowrate.

Since the solvent flowrate is unknown, the design target, i.e. the solubility multiplied by the solvent flowrate:

\[
SF_w = (X_1 - X_2)F_w \tag{8}
\]

Solution of this problem is the reverse of a simulation problem. A conventional simulation problem requires the specification of the input conditions, i.e. \( F_w, X_1, S \) and \( F_s \) and then the resulting outlet composition \( X_2 \) can be calculated. By specifying the desired outlet composition and solving for the solvent capacity instead, the simulation problem is reversed.

The second problem, i.e. the identification of candidate solvents, which match the design target, is a reverse property prediction problem. Conventional property prediction calculates the physical properties of a compound based on molecular structure. A reverse property prediction identifies molecular structures possessing a given set of properties. Reverse property prediction is often referred to as Computer Aided Molecular Design (CAMD) [9].

In this reverse property prediction problem, it is possible to use a database, liquid activity coefficient models as well as correlations such as solubility parameters or any other suitable model in order to determine \( S \) and then select various values of \( F_w \) that matches the target solvent capacity. Using a ranking approach based on, e.g. total solvent cost the optimal solution is identified. It is important to point out that solution of the reverse property prediction problem identifies all feasible solutions, thereby ensuring that the truly optimal solution can be found.

5. General solution strategy

The methodology for solving the integrated process and product design problems is divided in three parts. The different steps of the method are presented below: steps 1 and 2 constitute the input specification and model generation steps, step 3 formulates and solves the reverse simulation problem, while step 4 solves the reverse property prediction problem. Finally, step 5 identifies the optimal solution by employing a ranking approach.

1. Specify the synthesis/design problem in terms of known inputs and known outputs (for new process and product) and/or equipment parameters (for retrofit problems).
2. Select the unit operations to be considered and generate the corresponding individual process models (without the constitutive equations).
3. Formulate and solve the reverse simulation problem with the constitutive variables as the unknown (design) variables that match a specified design target (can be solved as optimization problem or simply as a reverse simulation problem).
4. Formulate and solve the reverse property prediction problem in order to determine the conditions of operation, flowsheet structure and/or product that match the target values identified in step 3.
5. Compute the performance index for all feasible solutions from step 4 and order them to determine the optimal solution.

The benefit of employing the reverse problem formulation technique is that by solving for the constitutive variables directly and thereby identifying the design targets, the solution becomes simpler since the (often complex) constitutive equations have been decoupled from the process model. It is important to point out that the solution strategy presented above is valid for new process synthesis/design problems as well as retrofit problems. The different problem types define the choice of equations and variables.

6. Definition of property clusters

To overcome the limitations encompassed when trying to track properties among process streams and units, the use of property-based clusters has been proposed [4]. The clusters are tailored to possess the two fundamental properties of inter- and intra-stream conservation, thus enabling the development of consistent additive rules along with their ternary representation. The clusters are obtained by mapping property relationships into a low dimensional domain, thus allowing for visualization of the problem. The clusters can be described as functions of the raw properties. The clustering approach utilizes property operators defined as

\[
\psi_j(P_M) = \sum_{i=1}^{N} \frac{F_{i,j}}{\sum_{i=1}^{N} F_{i}} \psi_j(P_{i}) = \sum_{i=1}^{N} x_i \psi_j(P_{i}) \tag{9}
\]

In Eq (9), \( \psi_j(P_{i}) \) is an operator on the \( j \)th property \( P_{i} \) of stream \( i \). The property operator formulation allows for simple linear mixing rules, i.e. the operators correspond to the actual properties, or the operators may describe functional
relationships of the properties, e.g. for density, where the resulting property of mixing two streams is given as the inverse of the summation over the reciprocal property values multiplied by their fractional contribution (s). The property operators are converted to dimensionless variables by division by an arbitrary reference, which is appropriately chosen such that the resulting dimensionless properties are of the same order of magnitude:

\[ \Omega_j = \frac{\psi_j(F_j)}{y_j^s} \]  

An augmented property index (AUP) for each stream \( s \) is defined as the summation of all the dimensionless property operators:

\[ \text{AUP}_s = \sum_{j=1}^{NP} \Omega_j \]  

The property cluster for property \( j \) of stream \( s \) is defined as

\[ C_j^s = \frac{\Omega_j}{\text{AUP}_s} \]  

Incorporating these clusters into the mass integration framework [5] enables the identification of optimal strategies for recovery and allocation of plant utilities. Process insights are covering separation and recycle problems. Current efforts are focused on extending the methodology to include reactive systems as well.

### 7. Model derivations

Fig. 3. Mixer schematic.

In order to utilize the possibilities of visualizing process synthesis/design problems by means of property clusters it is necessary to have models for different unit operations reformulated in terms of such clusters. In the following, the fundamental composition based balance models are derived and reformulated to obtain cluster-based models, which satisfy the original mass balance equations. In this contribution, the models are derived for mixing and splitting only, thus covering separation and recycle problems. Current efforts are focused on extending the methodology to include reactive systems as well.

#### 7.1. Cluster formulation of mixer model

Any mixing operation can be described by a series of binary mixing processes, i.e. where two feed streams are mixed to obtain one product stream (Fig. 3). The individual component balances for component \( i \) may be written as

\[ F_{1y_i} + F_{2y_i} = F_{My_i} \]

Introducing flowrate fractions and rearranging to find the mixture compositions:

\[ y_{Mi} = x_1 y_{i1} + x_2 y_{i2}; \quad x_1 = \frac{F_1}{F_M}, x_2 = \frac{F_2}{F_M} \]

The augmented property index for the mixture can be calculated by summation of the dimensionless property operators, as defined by Eq. (11):

\[ \text{AUP}_M = x_1 \text{AUP}_1 + x_2 \text{AUP}_2 \]

Eq. (16) shows that a lever–arm rule exists for calculating the AUP index for a mixture of two streams using only the feed stream properties.

Employing the cluster definition given in Eq. (12) the mixture clusters may be calculated. Combining Eqs. (12) and (15) yields

\[ C_{Mi} = x_1 \frac{C_{j1}}{\text{AUP}_1} + x_2 \frac{C_{j2}}{\text{AUP}_1} = \beta_1 C_{j1} + \beta_2 C_{j2} \]

Once again a lever–arm expression is obtained to determine the cluster values of the mixture using only the feed stream information. This was a desired feature of the clusters (inter-stream conservation), as it provides the option of consistent additive rules to be used within a ternary representation of the problem. A cluster composition corresponding to the fractional (relative arm) contributions of the two individual clusters to the mixture cluster is given in Eq. (17) by the \( \beta \) parameter. It must be emphasized at this point that the
cluster based mixing model represented by Eq. (17) originates from the original mass balance equation, thus any design calculations carried out using Eq. (17) will satisfy the mass balance (Table 1).

Once the mixing operation has been solved in the cluster domain, the result must be converted back to the property domain and finally the corresponding compositions must be identified. After the conversion to properties the following equations is satisfied:

\[ \sum_{i=1}^{NC} y_{i,jF} = 1 \]  \hspace{1cm} (19)

A degree of freedom analysis of the system shows that the number of variables (unknowns) is NC, while the number of equations is \( j + 1 \). Thus, the degrees of freedom are \( NC - (j + 1) \). This means that for \( NC > j + 1 \) the system cannot be uniquely solved. The reason for this result is that a high dimensional system is mapped to a system of only \( j \) dimensions. When trying to return to the composition space for \( NC > j + 1 \), the solution is not unique, since infinite parameter combinations exist that obey the above equations.

However only ONE solution exists that also satisfies the mass balance equations. Therefore, by fixing \( NC - (j + 1) \) compositions from the mass balance equations, this unique solution of the original \( NC \times NC \) system is guaranteed. Any set of components may be chosen for which to fix the compositions, however in order to have a common rule base, the components \( i \in [j + 2, NC] \) are chosen.

It should be noted that by including the mass balance equations as constraints, the above described problem could also be solved uniquely by mathematical optimization.

7.2. Cluster formulation of splitter model

A procedure analogous to the one performed on the fundamental mixer model, can be performed for a component splitter unit. Any splitting operation can be described by a series of binary splitting processes, i.e. where one feed stream is split to obtain two product streams (Fig. 4).

The individual component balances for component \( i \) may be written as

\[ F_{i,3F} = F_{i,3} + F_{i,3} \]  \hspace{1cm} (20)

Introducing a product flowrate fraction and rearranging yields

\[ \sum_{j=1}^{NC} y_{i,jF} = x_{i,jF} + x_{i,jF} \]  \hspace{1cm} (21)

We now introduce the component split factors:

\[ S_i = \frac{F_{i,3F}}{F_{i,3}} \]  \hspace{1cm} (22)

Summation over all components yields the product flowrate fraction:

\[ \sum_{i=1}^{NC} S_i y_{i,jF} = \sum_{i=1}^{NC} \sum_{j=1}^{NC} y_{i,jF} = x_{i,jF} \]  \hspace{1cm} (23)

Combining Eqs. (21) and (22) yields

\[ S_i = \frac{F_{i,3F}}{F_{i,3}} \]  \hspace{1cm} (24)

For visualization purposes only 3 properties are used. Eq. (21) can be rewritten in terms of dimensionless property operators as follows:

\[ \Omega_{iF} = \sum_{i=1}^{NC} \sum_{j=1}^{NC} y_{i,jF} \]  \hspace{1cm} (25)

A similar expression can be obtained by reformulating Eq. (24) in terms of dimensionless property operators:

\[ \Omega_{iF} = \Omega_{iF} \]  \hspace{1cm} (26)

In Eq. (26), a pseudo dimensionless property operator \( \Omega_{iF} \) is introduced. This parameter describes the relationships between the properties of product stream 2 as a function of the properties of the feed stream. It should be noted that \( \Omega_{iF} \) is a function of known variables only, i.e. the split factors, feed stream composition and the pure component property values, and in principle \( \Omega_{iF} \) can be described as a property split factor. This new parameter is easily calculated (the annotation for pure component properties, which are marked by a (*), uses two indices, i.e. \( j \) is the property ID, while \( i \) denotes the component ID):

\[ \Omega_{iF} = \sum_{j=1}^{NC} S_i \]  \hspace{1cm} (27)
Table 2
Calculation sequence for identification of product clusters from splitting operation

<table>
<thead>
<tr>
<th>Step</th>
<th>Description</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Split1</td>
<td>Calculate dimensionless feed stream property values</td>
<td>(10)</td>
</tr>
<tr>
<td>Split2</td>
<td>Calculate feed stream AUP index</td>
<td>(11)</td>
</tr>
<tr>
<td>Split3</td>
<td>Calculate ternary cluster values for feed stream</td>
<td>(12)</td>
</tr>
<tr>
<td>Split4</td>
<td>Calculate flowrate distribution</td>
<td>(23)</td>
</tr>
<tr>
<td>Split5</td>
<td>Calculate the property split factors</td>
<td>(27)</td>
</tr>
<tr>
<td>Split6</td>
<td>Calculate dimensionless property values for products</td>
<td>(28) and (29)</td>
</tr>
<tr>
<td>Split7</td>
<td>Calculate AUP index for product streams (30) and (31)</td>
<td>(32) and (33)</td>
</tr>
</tbody>
</table>

Eq. (26) can be rearranged to provide an expression for the properties of product stream 3:

\[
\Omega_j^3 = \frac{\Omega_j^2 S_j^{\text{split}}}{x_3} \sum_{j=1}^{NC} \frac{\Omega_j^2 - \Omega_j S_j^{\text{split}}}{x_3} \]

(28)

Inserting this expression in Eq. (25) provides the corresponding expression for the properties of product stream 2:

\[
\Omega_j^2 = \frac{\Omega_j S_j^{\text{split}}}{x_2} = \frac{\Omega_j^3 S_j^{\text{split}}}{x_3} \sum_{j=1}^{NC} \frac{\Omega_j^3 - \Omega_j S_j^{\text{split}}}{x_3} \]

(29)

The augmented property index for the two product streams can be calculated by summation of the dimensionless property operators, as defined by Eq. (11):

\[
\text{AUP}_2 = \sum_j \Omega_j S_j^{\text{split}} = \frac{1}{x_2} \sum_j \Omega_j S_j^{\text{split}} \]

\[
\text{AUP}_3 = \sum_j \Omega_j S_j^{\text{split}} = \frac{1}{x_3} \sum_j (\Omega_j^2 - \Omega_j S_j^{\text{split}}) \]

(30)

(31)

Employing the cluster definition in Eq. (12) the product clusters are calculated:

\[
C_j^2 = \frac{\Omega_j S_j^{\text{split}}}{\text{AUP}_2} = \frac{1}{x_2} \sum_j \Omega_j S_j^{\text{split}} \]

(32)

\[
C_j^3 = \frac{\Omega_j S_j^{\text{split}}}{\text{AUP}_3} = \frac{1}{x_3} \sum_j (\Omega_j^2 - \Omega_j S_j^{\text{split}}) \]

(33)

An interesting feature of the splitter model is that the resulting product clusters are independent of the flowrate distribution even though the stream properties are functions of \(x_r\). Furthermore, the conservation of the clusters is achieved, since the two product clusters described by Eqs. (32) and (33), add up to the property cluster for the original feed stream.

For a given set of component split factors \(S_j\), the calculation sequence given in Table 2 yields the ternary cluster values for the two product streams. The sequence in Table 2 includes the calculation of the product stream properties and AUP indices as these are necessary for converting the solution back to composition space. It should be noted however that the product cluster values could have been calculated using only the feed stream information and the component split factors. This means that steps 6 and 7 in Table 2 are not required for the cluster based solution but generate the necessary data for the composition based solution.

By repeating the calculation sequence for all parameter combinations of \(S_j\) ranging from 0 to 1 in suitable intervals, e.g. with a step size of 0.1, the feasibility region for the splitting operation is obtained. It should be noted that any separation technique and conditions of operation will result in ternary clusters within this region, thus it can be used for identifying the design targets, i.e. the set of separation factors. Furthermore, this discretization procedure only serves as a simple means of determining the graphical location of the feasibility region. It is also possible to derive an analytical expression for the boundaries of this region.

Once the splitting operation has been solved in the cluster domain, the results must be converted back to the property domain and finally the corresponding compositions must be identified. After the conversion to properties the following equations, where each property \(j\) of the products is a function of composition, are given. Furthermore the compositions in each product stream must sum to unity:

\[
\Omega_j^2 = f_j(y_j^2); \quad i \in [1, \text{NC}] \]

(33)

\[
\Omega_j^3 = f_j(y_j^3); \quad i \in [1, \text{NC}] \]

(34)

\[
\sum_{i=1}^{\text{NC}} y_i^2 = 1 \]

(35)

\[
\sum_{i=1}^{\text{NC}} y_i^3 = 1 \]

(36)

A degree of freedom analysis of the system shows that the number of variables (unknowns) is \(2^N \text{NC}\), while the number of equations is \(2^N \text{NC} - 2^N (j + 1)\). Thus, the degrees of freedom are \(2^N \text{NC} - 2^N (j + 1)\). It could be argued that since all the component split factors are known, the compositions of one product stream is also known. However, to obtain square matrices, only the compositions for components \(i \in [j + 2, \text{NC}]\) are calculated by using the split factors. The corresponding compositions in the other product stream are fixed from the mass balance equations, thus yielding \(2^N \text{NC} \times \text{NC}\) systems, which can be uniquely solved to obtain the product compositions.

8. Illustrative example

The problem to be solved involves choosing the correct sequence of mixers and splitters for matching a set of target values. It should be noted that the example is based on
purely theoretical values, which are not related to any specific components or properties. The purpose of this example is solely to illustrate and validate the use of mixing and splitting operations for solving design problems in cluster space.

8.1. Problem formulation

The objective is to match a set property values for a product stream by mixing and splitting two feed streams accordingly. Three properties $P_1$, $P_2$ and $P_3$ have been found to be able to characterize the streams. The initial inputs, i.e. pure component property values, property references, stream summaries as well as the desired property targets are given in Tables 3–5.

8.2. Visualization of problem

Conversion of the feed stream and property target information to clusters is achieved by employing Eqs. (10)–(12).

The resulting cluster mapping is given in Fig. 5. Since all mixing operations within the cluster diagram are described by a straight line, it is evident from Fig. 5 that it is NOT possible to mix the two feed streams in any ratio to match the property targets. Therefore, it is necessary to split at least one of the streams. The feasibility regions are identified by employing the calculation sequence outlined in Table 2 using a parameter step size of 0.1.

8.3. Identification of operating sequence

It is desired to use a minimum number of processing units, thus we decide to split feed stream 2 and mix one of

<table>
<thead>
<tr>
<th>Component $i$</th>
<th>Pure component properties</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$P_1^*$</td>
</tr>
<tr>
<td>1</td>
<td>50</td>
</tr>
<tr>
<td>2</td>
<td>65</td>
</tr>
<tr>
<td>3</td>
<td>76</td>
</tr>
<tr>
<td>4</td>
<td>100</td>
</tr>
<tr>
<td>5</td>
<td>118</td>
</tr>
<tr>
<td>6</td>
<td>75</td>
</tr>
</tbody>
</table>

Table 3
Pure component property data

<table>
<thead>
<tr>
<th>Feed stream summaries</th>
</tr>
</thead>
<tbody>
<tr>
<td>Data</td>
</tr>
<tr>
<td>$y_1^s$</td>
</tr>
<tr>
<td>$y_2^s$</td>
</tr>
<tr>
<td>$y_3^s$</td>
</tr>
<tr>
<td>$y_4^s$</td>
</tr>
<tr>
<td>$y_5^s$</td>
</tr>
<tr>
<td>$y_6^s$</td>
</tr>
<tr>
<td>Flowrate</td>
</tr>
</tbody>
</table>

Table 4
Feed stream summaries

<table>
<thead>
<tr>
<th>Property targets and reference values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Property</td>
</tr>
<tr>
<td>$P_1$</td>
</tr>
<tr>
<td>$P_2$</td>
</tr>
<tr>
<td>$P_3$</td>
</tr>
</tbody>
</table>

Table 5
Property targets and reference values
the products with feed stream 1. Drawing a straight line between the cluster points for feed stream 1 and the desired product provides the operating line for the mixing operation. The stream to be mixed with feed stream 1 to match the target MUST lie on this line in such a location that the target cluster is between the two streams to be mixed. Furthermore the stream must also be within the split feasibility region of feed stream 2. In Fig. 6, the solid black line represents the operating line for feasible mixing agents that match the property target. However, the only cluster points that also satisfy the feasibility constraints are designated by the grey section. In this example, we decide to split feed stream 2 in such a way that the minimum arm of feed stream 1 is used. This means that when employing lever-arm analysis at the mixing point (target point), the arm representing feed stream 1 should be minimized. Using this objective, the optimal point to be mixed with feed stream 1 is the point located just on the border of the feasibility region in Fig. 6. When one of the products of a splitting operation is defined the other product will be located on a straight line from the first product and extended through the feed point. How far away from the feed point the second product is located depends on the choice of split factors. In this example any set of component split factors resulting in the first product are valid solutions (Fig. 7).

A powerful feature of the cluster-based mapping diagram is the ability to directly obtain the corresponding process flowsheet. This is possible because the formulation of the clusters and the unit operation models satisfy the overall balance equations. It should be emphasized that once the problem was reformulated in terms of cluster all the design calculations were performed graphically and composition free (Fig. 8).

Along with the process flowsheet, the stream summaries in terms of ternary cluster values and flowrates along with flowrate distributions for the two units are available. Employing the calculation sequence outlined earlier, allows for back calculating the compositions in each stream from the

Table 6 Stream summary using compositions

<table>
<thead>
<tr>
<th>Stream ID</th>
<th>S1</th>
<th>S2</th>
<th>S3</th>
<th>S4</th>
<th>S5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed 1</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Feed 2</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Target</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td></td>
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<td>1</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Flowrate</td>
<td>10</td>
<td>150</td>
<td>20.25</td>
<td>129.75</td>
<td>30.25</td>
</tr>
</tbody>
</table>
cluster solution. The stream summary in terms of compositions is given in Table 6.

Once again it should be pointed out that all the design calculations were performed on a composition free basis. The algorithm solves the process design problem in terms of property values providing design targets for the constitutive variables. In this particular example, the design targets obtained by the reverse problem formulation are the component split factors. The second reverse problem consists of identifying the separation technique capable of matching these targets. In this contribution solution of the constitutive equations to find the matching splitting operation will not be investigated further.

9. Case study: VOC recovery from metal degreasing process

The metal degreasing process presented in Fig. 9 uses a fresh organic solvent in the absorption column and another one in the degreaser. Currently, the off-gas VOCs evaporating from the degreasing process are simply
flared, leading to economic loss and environmental pollution.

In this case study, the objective is to explore the possibility of condensing and reusing the off-gas VOCs, thus optimizing the usage of fresh solvents and simultaneously identify candidate solvents for both units. Three properties are examined to determine the suitability of a given organic process fluid for use in the absorber and degreaser; sulfur content (for corrosion considerations), density (for hydrodynamic aspects) and Reid vapor pressure (for volatility, makeup and regeneration). The solvents to be synthesized are pure component fluids, thus the sulfur content of these streams is zero.

The constraints on the inlet conditions of the feed streams to the absorber and degreaser, respectively, are given in Table 7, while the unit feed constraints were converted to cluster values yielding the two regions for the absorber and degreaser, respectively. The cluster data was plotted and the feasible mixing paths identified. Since the fresh process fluids contain no sulfur, any feasible solution will be on the C2–C3 axis. Lever–arm analysis is employed to identify the minimum flow solutions.

At a condensation temperature of 280 K the condensate flowrate is 30.0 kg/min. Since the minimum flowrate requirement for the degreaser feed is 36.6 kg/min, the target for minimum fresh solvent usage is 6.6 kg/min assuming that a suitable solvent can be identified. Lever–arm analysis is employed to identify the minimum feasible flowrate, i.e. for a solvent that when mixed with the condensate actually satisfies the constraints for the degreaser. This analysis showed that of the feasible mixing paths the minimum feasible flowrate of the fresh solvent is 11.8 kg/min. In order to investigate whether a better solution exists, the same analysis was performed for a condensation temperature of 285 K. At this temperature the condensate flowrate is slightly reduced (29.5 kg/min), thus resulting in a target for minimum fresh solvent usage of 7.1 kg/min. When performing the lever–arm analysis to identify the minimum feasible solvent flowrate the result was also 7.1 kg/min, i.e. the target can be matched at this condensation temperature. It should be noted that using this approach the flowrate of the fresh material has been reduced by approximately 80%.

The analysis showed that the cluster solutions to the degreaser problem correspond to the degreaser points on the C2–C3 axis. Since all the condensate has been recycled to

<table>
<thead>
<tr>
<th>Unit</th>
<th>Absorber</th>
<th>Degreaser</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfur content (wt.%)</td>
<td>0.0 &lt; P1 &lt; 0.1</td>
<td>0.0 &lt; P1 &lt; 1.0</td>
</tr>
<tr>
<td>Density (kg/m³)</td>
<td>530 &lt; P2 &lt; 610</td>
<td>555 &lt; P2 &lt; 615</td>
</tr>
<tr>
<td>Reid vapor pressure (atm)</td>
<td>1.5 &lt; P3 &lt; 2.5</td>
<td>2.1 &lt; P3 &lt; 4.0</td>
</tr>
<tr>
<td>Flowrate (kg/min)</td>
<td>4.4 &lt; F &lt; 6.2</td>
<td>36.6 &lt; F &lt; 36.8</td>
</tr>
</tbody>
</table>

Table 7: Process unit feed constraints.
degreaser, the solution for the absorber is a simple molecular design problem.

Using the information obtained from the cluster diagram mapping analysis a computer-based tool ProCAMD [8] was invoked to synthesize candidate process fluids. Not allowing phenols, amines, amides or compounds containing silicon, sulfur or halogens, due to safety and health considerations, reduced the search space. The CAMD algorithm [9] yielded a series of candidate solvents for each of the process units.

Of the candidate compounds identified by the software, iso-pentane was chosen for the absorber and n-butane for the degreaser.

It is important to point out that the case study is solved in terms of properties only, i.e. no component information or compositions were needed to obtain the design targets. The reason for this is that experimental data was available for the properties of the individual streams. Therefore, it is straightforward to convert the property values to cluster
values using Eqs. (10)–(12). The unit feed regions are calculated analogously to the feasibility regions for stream splitting (see Table 2); however instead of calculating cluster points for all parameter combinations of split factors, parameter combinations of the property values describing the unit feed constraints are used (Fig. 12).

The design calculations follow the methodology outlined previously, furthermore in terms of reverse simulation, the conditions of operation (intensive variables) for the condenser, i.e. condensation temperature, is identified, instead of the unit operation. The objective of the case study was to investigate the possibilities of using condensation of the degreaser off-gas as a substitute solvent, thus the unit operation was fixed, however the operating conditions were not known.

10. Conclusions

In this work, a novel framework for solving process and product design problems has been introduced. The methodology is based on reformulating the conventional forward problems into two reverse problem formulations by decoupling the constitutive equations from the balance and constraint equations. The first reverse problem is the reverse of a simulation problem, where the process model is solved in terms of the constitutive (design) variables, thus providing the design targets. The second reverse problem (reverse property prediction) solves the constitutive equations to identify unit operations, operating conditions and/or products. The main advantage of this approach is that the application range of the models has been expanded, while the problem solution has become simpler, flexible and visual. An inherent benefit of the reduction in model complexity is that the solution of the problem does not depend on the ability of the solver to handle complex process model equations. Visualization of the problem is achieved by employing recently developed property clustering techniques, which allows a high-dimensional problem to be visualized in two or three dimensions. The clusters are tailored to have the attractive features of intra-stream and inter-stream conservation, thus enabling the development of consistent additive rules along with their ternary representation. A cluster-based mapping diagram allows graphical representation of the process streams and units.

It should be emphasized that for visualization purposes the methodology is limited to the use of three property-based clusters. This means that only three property operators can be used, however this does not restrict the methodology to only three properties as well. Even if more than three properties are practically relevant for adequate description of the process, as it is linear in terms of the clusters, because the non-linearities are hidden in the property operators.

References


