Complete Separation System Synthesis of Fractional Crystallization Processes

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Abstract

A methodology is presented for the synthesis of fractional crystallization processes. The methodology is based on the construction of four networks. The first network is based on the identification of feasible thermodynamic states. In this network the nodes correspond to multiple saturation points, solute intermediate, process feeds and end products. The second network is used to represent the variety of tasks that can be performed at each multiple saturation point. These tasks include cooling crystallization, evaporative crystallization, reactive crystallization, dissolution, and leaching. Heat integration is included using a heat exchanger network which can be regarded as a transhipment problem. The last network is used to represent filtration and cake washing alternatives. The cake wash and task networks are modelled using disjunctive programming and then converted into a mixed integer program. The method is illustrated through the design of a salt separation example.

1. Introduction

There are two major approaches for the synthesis of crystallization-based separation. In one approach, the phase equilibrium diagram is used for the identification of separation schemes (For example Cisternas and Rudd, 1993; Berry et al., 1997). While these procedures are easy to understand, they are relatively simple to implement only for simple cases. For more complex systems, such as multicomponent systems and multiple temperatures of operation, the procedure is difficult to implement because the graphical representation is complex and because there are many alternatives to study. The second strategy is based on simultaneous optimization using mathematical programming based on a network flow model between feasible thermodynamic states (Cisternas and Swaney, 1998; Cisternas, 1999; Cisternas et al. 2001; Cisternas et al. 2003).

In crystallization and leaching operations, filtration, washing and drying are often required downstream to obtain the product specifications. For example, usually filter cake must be washed to remove residual mother liquor, either because the solute is valuable or because the cake is required in a semiclean or pure form. These issues have been discussed by Chang and Ng (1998), who utilized heuristic for design purposes. The objective of this study is to address these issues using mathematical programming. This work constitutes part of our overall effort on the synthesis of fractional crystallization processes. Drying is not included in this method because, as it normally
does not involve a recycle stream, the dryer can be considered as a stand-alone operation.

2. Model Development

2.1. Networks for Fractional Crystallization

The model proposed in this paper is composed of four networks: (1) the thermodynamic state network, (2) the task network, (3) the heat integration network, and (4) the cake wash network. The first three networks have been described in our previous works; therefore, emphasis here is given to the cake wash network.

The first network is based on the detection of feasible thermodynamic states. Using equilibrium data for a candidate set of potential operating point temperatures, a thermodynamic state network flow model is create to represent the set of potential separation flowsheet structures that can result. This representation was presented by Cisternas and Swaney(1998) for two solutes systems, by Cisternas(1999) for multicomponent systems, and by Cisternas et al.(2003) for metathetical salt. Figure 1 shows the thermodynamic state network representation for a two solute system at two temperatures. The structure contains feeds, two multiple saturation points, and products.

The second network, which is also shown in Figure 1, is the task network (Cisternas et al. 2001). Each multiple saturation state can be used for different tasks depending on the condition/characteristic of the input and output streams. For example, if solvent is added to an equilibrium state, the task can be: (1) a leaching step, if the feed is solid; (2) a cooling crystallization step, if the feed is a solution with a higher temperature; or (3) a reactive crystallization step, if the feed is a crystalline material that decomposes at this temperature or in the solution fed to this state (for example, the decomposition of carnallite to form potassium chloride).

The third network, a heat exchange network, can be regarded as a transhipment problem as in Papoulias and Grossmann (1983). This transhipment problem can be formulated as a linear programming problem. In this representation hot streams and cold streams corresponds to the arcs in the thermodynamic state network.

The fourth network is the cake wash network. Cake washing can be accomplished by two methods: (a) The cake may be washed prior to removal from the filter by flushing it with washing liquor. This can be done with both batch and continuous filters. (b) the cake may be removed from the filter and then washed in a mixer. The wash suspension obtained may then be separated with the filter. Figure 2 shows both alternatives for removing the residual mother liquor of concentration \( y_{c,1} \). Figure 2 shows only one stage, but washing may be performed in one or several stages on either batch or continuous filters. In this work countercurrent washing is not considered. As a result, the first stage provides the most concentrated solution and the last stage provides the least. If operation states are near-equilibrium states, then mother liquor concentration in the cake is substantially that of a saturated solution at the final temperature in the process.

2.2. Mathematical Formulation

Having derived the networks for the separation problem, a mathematical programming
formulation is presented for each network to select the optimum flowsheet alternative of

![Diagram of Thermodynamic State Network](image1)

**Figure 1. Thermodynamic state network and task network**

![Diagram of Cake Wash Network for Stage e](image2)

**Figure 2. Cake wash network for stage e.**

the separation sequence.

The mathematical formulation for the thermodynamic state network is the same as that developed by Cisternas (1999) and Cisternas et al. (2003). Here a brief description is given. First, the set of thermodynamic state nodes will be defined as: \[ S = \{ s, \text{ all nodes in the system} \} \]. This includes feeds, products, multiple saturation points or operation points, and intermediate solute products. The components, solutes and solvents, will be denoted by the set \[ I = \{ i \} \]. The arcs, which denote streams between nodes, will be denoted by \[ L = \{ l \} \]. Each stream \[ l \] is associated with the positive variable mass flow rate \[ w_l \] and the parameter \[ x_{li} \] giving the fixed composition of each component in the stream. The constraints that apply are: (a) Mass balance for each component around multiple saturation and intermediate product nodes,
\[
\sum_{i \in S_q(l)} w_i \cdot x_i \cdot x_i - \sum_{i \in S_{in}(l)} w_i \cdot x_i \cdot x_i - \sum_{i \in S_{out}(l)} w_i \cdot h \cdot x_i \cdot x_i = 0 \quad s \in S_{in}, i \in I
\]

where \(L_q\) is the subset of \(L\) of solid stream product, \(h_i\) is the mass ratio of residual liquid retained in the cake pores to the solid product \(l\), and \(x_{ij}\) is the concentration of the mother liquid in equilibrium with solid product \(l\). Also \(S_{in}(s)\) and \(S_{out}(s)\) are the sets of input and output streams to node \(s\).

(b) Specification for feeds flow rates \(\sum_{(s,I)} F_{s,i} = \sum_{(s,F)} C_{s,i}\), where \((s,I)\) and \((s,F)\) are the desired flow rates of specie \(i\) in feed \(s\).

The heat integration network follows the approach presented by Papoulos and Grossmann(1983). First, it is considered that there is a set \(K=\{k\}\) of temperature intervals that are based on the inlet temperatures of the process streams, highest and lowest stream temperatures, and of the intermediate utilities whose inlet temperatures fall within the range of temperatures of the process streams. The only constraints that apply are heat balances around each temperature interval \(k\):

\[
R_k = R_{k-1} + \sum_{m \in V} Q_m^k + \sum_{n \in W} Q_n^k = \sum_{i \in H_k} w_i (C_i \Delta T)_h^k + \sum_{i \in C_k} w_i (C_i \Delta T)_c^k \quad k \in K
\]

where \(Q_m^V\), \(Q_n^W\), and \(R_k\) are positive variables that represent heat load of hot utility \(m\), heat load of cold utility \(n\), and heat residual exiting interval \(k\), respectively. \((C_i \Delta T)_h^k\) and \((C_i \Delta T)_c^k\) are known parameters that represent the heat content per unit mass of hot stream \(l \in H_k\) and cold stream \(l \in C_k\) in interval \(k\). \(H_k\), \(C_k\), \(V_k\) and \(U_k\) are the hot stream, cold stream, hot utility and cold utility set respectively in interval \(k\).

A task network is constructed for each multiple saturation point node \(s\). The mathematical formulation, which is close to that in Cisternas et al. (2001), includes mass and energy balance, logic relations to select the task based on input/output stream properties, and cost evaluations. The formulation use disjunctive programming.

A cake wash network is constructed for each solid stream product \(l \in L_q\). Let \(E(l)=\{e\}\) define the set of washing/reslurry stages in the solid stream product \(l \in L_q\). The variables are defined as follows: \(y_{l,e,i}\) is the concentration of species \(i\) in the residual mother liquor of the solid stream \(l\) at the output of wash/reslurry stage \(e\). \(z_{l,e,i}\) and \(r_{l,e,i}\) are the input and output concentration in the washing liquid for the solid stream \(l\), at stage \(e\). \(y_{pw_{l,e,i}}, y_{pr_{l,e,i}}, y_{mw_{l,e,i}}, y_{mr_{l,e,i}}, y_{rw_{l,e,i}}, y_{rr_{l,e,i}}\) are the concentration of the internal streams in stage \(e\) (see figure 2).

The wash efficiency parameter, \(E_{w_{l,e,i}}\) for specie \(i\) in solid stream \(l\) at the stage \(e\) can be defined as \(E_{w_{l,e,i}} = (ymw_{l,e,i} - yp_{l,e,i})/(rw_{l,e,i} - yp_{l,e,i})\) for \(l \in L_q, e \in E(l), i \in I\). The first two constraints in eq. (3) bellow are the efficiency constraint for the wash and reslurry/filter steps. Note that the efficiency for perfect mixing in the wash mixer is equal to 1. The last two constrains in Eq. (3) are the mass balances for specie \(i\) at the stage \(e\) of washing solid stream \(l\).

\[
\begin{align*}
E_{r_{l,e,i}} - Er_{l,e,i} - Er_{l,e,i} - ypr_{l,e,i} + ypr_{l,e,i} &= 0 \\
E_{w_{l,e,i}} - Er_{l,e,i} - ypw_{l,e,i} - ymw_{l,e,i} + ypw_{l,e,i} &= 0 \\
E_{r_{l,e,i}} - Er_{l,e,i} - ypr_{l,e,i} + ypr_{l,e,i} &= 0 \\
E_{w_{l,e,i}} - Er_{l,e,i} - ypw_{l,e,i} - ymw_{l,e,i} + ypw_{l,e,i} &= 0
\end{align*}
\]
This logical relation is rewritten as mixed-integer linear equations. The concentration of the last stage \( e' \) must satisfy the impurity level \( IL_{e'} \), this is \( y_{l,e} h_l \leq IL_{e'} \) for \( l \in Lq, i \in I \).

The objective function is to minimize the venture cost. The following equation can be used as an objective function,

\[
\min \sum_{i \in \mathcal{P}} \sum_{t \in \mathcal{T}} (FC_i + VC_i + c_{\ell} Q_{\ell}^C + c_{\ell} Q_{\ell}^S + \sum_{s \in \mathcal{S}} c_s Q_{s}^C + \sum_{s \in \mathcal{S}} c_s Q_{s}^S + \sum_{l \in Lq} (Cf_{l,e} + Cv_{l,e}))
\]  

Eq. (5) represents the total cost given by the investment and utility cost. In this way, the objective function in Eq. (5), subject to constraints in Equations 1 to 4, defines a mixed integer linear programming problem. The numerical solution to the MILP problem can be obtained with standard algorithms. In Eq. (5) \( Q_{\ell}^C, Q_{\ell}^S, VC_i \) and \( FC_i \) are the heat loads of crystallization or dissolution, the heat loads of evaporation, and the variable costs and fixed costs for the equipment associated with task \( t \) of multiple saturation point \( s \).
3. Illustrative Example

This example considers the production of potassium chloride from 100,000 ton/year of sylvinite (47.7% KCl, 52.3% NaCl). Data are given in Cisternas et al. (2001). The solution found is shown in figure 3. The problem formulation in 293 equations and 239 variables (27 binary variables) was solved using OSL2 (GAMS). The optimal solution divides the feed into two parts. A sensitivity analysis shows that product impurity level and residual liquid retained level in the cake can affect the solution and cost by 20%.

![Diagram of sylvinite processing](image)

Figure 4. Solution for example.

4. Conclusions

The objective of this paper has been to present a method for determining the desired process flowsheet for fractional crystallization processes including cake washing. To achieve this goal, a systematic model was introduced consisting of four networks: the thermodynamic state network, the heat integration network, the task network, and the cake wash network. Once the representation is specified, the problem is modelled as a MILP problem. From the example, we can conclude that the model can be useful in the design and study of fractional crystallization processes. Result from the example indicates that product impurity level and the level of residual liquid retained in the cake can affect the optimal solution.

5. References


6. Acknowledgment

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