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Design and Optimization of Layer Crystallization Processes

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Abstract

A novel design method for layer crystallization of simple eutectic organic melts is presented. The design task is formulated in form of a general disjunctive program (GDP) with the aim of minimizing the energy demand of the process as an indicator of its economic potential. Different solution methods of the GDP are discussed under the aspect of layer crystallization being part of a more complex process flowsheet.

Keywords: Layer crystallization, hybrid separation processes, GDP

1. Introduction

Layer crystallization processes are often utilized for the separation of organic melts (Jancic, 1987). High selectivity, absence of solvents as well as applicability to temperature-sensitive substances are characteristic for these processes (Rittner and Steiner, 1985). However, to be able to retrieve more than one component as a pure substance, melt crystallization processes need to be combined with other unit operations, e.g. distillation, to form a hybrid separation process. Thus, a large number of process alternatives has to be considered.

In order to be able to evaluate different process flowsheets at an early design stage, a design method is needed, which can supply information about important operating parameters on the basis of few input variables, and therefore allows for a rough estimation of the economic potential. With such methods, a screening of all possible alternatives can be performed. As a result the costly variants can be dismissed at this stage whereas the promising alternatives need to be investigated more thoroughly.

For distillation processes shortcut methods for ideal and nonideal mixtures are well known, e.g. the rectification body method (RBM) (Bausa et al., 1998), the boundary value method (BVM) (Levy et al., 1985) or Underwood's method (Underwood, 1948). For melt crystallization processes such methods are not documented in the literature to our knowledge.

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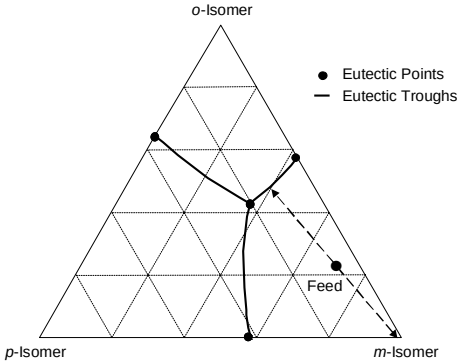

Figure 1: Polythermal phase diagram of a ternary isomeric mixture.

In this contribution such a shortcut model for layer melt crystallization processes is presented, which allows for an estimation of the energy demand on the basis of feed and product specifications. Furthermore, different solution methods for the arising GDP are discussed, taking into consideration that the overall goal is a reliable flowsheet optimization of hybrid separation processes consisting of distillation and layer crystallization.

2. Layer Crystallization

In layer crystallization a crystal layer is growing at a cooled surface. After a distinct crystallization time the solid-liquid separation is carried out simply by draining off the remaining liquid followed by re-melting of the crystal layer formed. Ideally, the gained product would be pure, but due to enclosed and adherent melt the crystal layer contains impurities. Therefore, more than one crystallization stage is needed to meet the required product purity.

2.1 Representation in the Phase Diagram

In Figure 1 the polythermal phase diagram of a ternary isomeric mixture is shown. The composition space is separated into three compartments by eutectics and eutectic troughs. These are the thermodynamic boundaries of the process on which one or more components co-crystallize. In each compartment only one component can be recovered as a pure product, e.g. for the feed indicated in figure 1 only the *m*-isomer will crystallize during cooling. Also, the product yield is limited by eutectics and eutectic troughs. During the crystallization process, the composition of the remaining liquid moves on a straight line away from the pure component. As soon as the composition touches on one of the thermodynamic boundaries, a second component will cocrystallize which is undesired in the purification process (e.g. Dye and Ng, 1995). Note that the straight line is not just a mass balance, but can be seen as analogues to residue curves for distillation processes.

2.2 Estimation of Energy Demand

The energy demand of a layer crystallization process can be considered as a measure for assessing cost. In the case of an ideal separation the energy demand $\dot{Q}_{LC}$ could simply

be calculated from the amount of crystals $\dot{m}_{cryst}$ produced, the enthalpy of fusion ΔH_m and the heat required for cooling the apparatus $\dot{Q}_{App}$ to

$$\dot{Q}_{LC} = \dot{m}_{cryst} \Delta H_m + \dot{Q}_{App} . \tag{1}$$

However, as the separation is not ideal the crystal layer formed contains impurities and more than one crystallization stage is needed to fulfil the required product purity. Wellinghoff and Wintermantel (1991) presented a methodology for the estimation of the energy demand in a crystallization cascade. First, they introduced the crystallization effort *K*, defined as the ratio of total amount of crystals produced to the amount of pure product $\dot{m}_{pp}$, which accounts for the existence of more than one stage:

$$K = \frac{\sum_j \dot{m}_{cryst,j}}{\dot{m}_{pp}} \quad , \qquad j = 1 \ldots N . \tag{2}$$

With this parameter, the calculation of the energy demand reads as

$$\dot{Q}_{LC} = \dot{m}_{pp} \Delta H_m K (1 + \frac{\dot{Q}_{App}}{Q_S}) , \tag{3}$$

where $\dot{Q}_{App} / \dot{Q}_S$ describes the ratio of heat required for cooling the apparatus to the heat of crystallization. An experimental estimation of this ratio by the authors led to the following relationship:

$$1 < \frac{\dot{Q}_{App}}{\dot{Q}_S} < 3 \tag{4}$$

From (3) it is obvious, that the specific energy demand $\dot{Q}_{LC} / \dot{m}_{pp}$ can be estimated if the crystallization effort *K* is known. Therefore, the mass flows and concentrations on each stage need to be calculated.

For better understanding of how to calculate those fluxes, let us first consider a binary simple eutectic system (Figure 2, left). For a given operating temperature *T* the composition of the remaining mother liquor on one stage can be calculated utilizing the equilibrium and summation equations. The solid composition can not be calculated with such an equilibrium relation, but as described by Franke et al. (2004), the amount of impurities in the crystal layer depends approximately linearly on the supercooling of the melt when constant freezing ratios are assumed. Thus, for a given operating temperature, the composition of the melt can also be determined if the constant of proportionality is known. Therefore, the crystallization effort can be calculated for any given temperature *T* in the binary case. When addressing the separation of ternary mixtures, one further assumption has to be made, since fixing the operating temperature does not yield a unique solution for solid and liquid compositions (Figure 2, right). Given that the impurities of the crystal layer derive from enclosed and adherent melt, the overall solid composition can be considered as a mixture of pure component and melt. Therefore we assume that the mass balance of a crystallization stage can be represented by a straight line through feed and pure product in composition space.

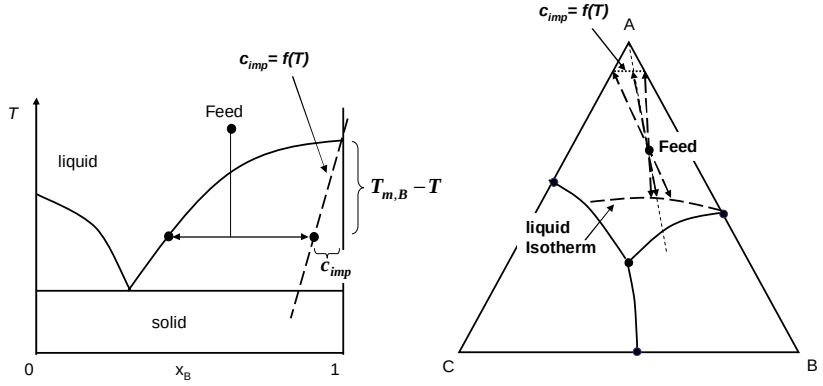

Figure 2: Determination of the compositions on a single crystallization stage for binary (left) and ternary (right) mixtures

Now, the crystallization effort, and therefore the specific energy demand, can also be estimated for simple eutectic, ternary mixtures at some given operating temperature. Since product recovery and product purity are conflicting targets, both affected by the operating temperature, a nonlinear programming problem has to be solved with the objective to minimize the energy demand of a crystallizer with a given structure (number of stages N, feed stage N_F). However, looking at the definition of the crystallization effort K (2) reveals that the structure of the crystallization cascade is also affecting the specific energy demand and therefore is subject to optimization as well. Thus, the NLP develops into to the following general disjunctive program (GDP) (for nomenclature see figure 3):

$$\min_{\boldsymbol{T},\boldsymbol{Y}} \dot{Q}_{spec}$$

$$\begin{aligned} s.t. \quad & \boldsymbol{F}(\boldsymbol{L}, \boldsymbol{xl}, \boldsymbol{S}, \boldsymbol{z}, \boldsymbol{T}) = 0 \\ & \boldsymbol{G}(\boldsymbol{L}, \boldsymbol{xl}, \boldsymbol{S}, \boldsymbol{z}, \boldsymbol{T}) \le 0 \end{aligned}$$

$$\begin{bmatrix} Y_i \\ f_i(\boldsymbol{L}, \boldsymbol{xl}, \boldsymbol{S}, \boldsymbol{z}, \boldsymbol{T}) = 0 \\ g_i(\boldsymbol{L}, \boldsymbol{xl}, \boldsymbol{S}, \boldsymbol{z}, \boldsymbol{T}) \le 0 \end{bmatrix} \vee \begin{bmatrix} \neg Y_i \\ \\ B_i(\boldsymbol{L}, \boldsymbol{xl}, \boldsymbol{S}, \boldsymbol{z}, \boldsymbol{T}) = 0 \end{bmatrix}, \quad i = 1, \ldots, N_{\max} \tag{5}$$

$$\boldsymbol{\Omega}(\boldsymbol{Y}) = True, \quad Y_i \in \{True, False\}.$$

In the GDP formulation (5), **F** and **G** are model equations which apply regardless of the structure of the crystallization cascade (e.g. overall mass balance), **f** and **g** are the model equations for the crystallization stages (mass and component balances, phase equilibrium, etc.) and **B** represents the bypass equations (e.g. $\boldsymbol{xl_i} = \boldsymbol{xl_{i-1}}$ *or* $\boldsymbol{z_i} = \boldsymbol{z_{i+1}}$) which apply if a stage is not existing, i.e. Y_i = *False* (Oldenburg 2005). The logic constraints $\boldsymbol{\Omega}$ ensure that equal configurations will only be accounted for once and also enforce the feed stage to be existing.

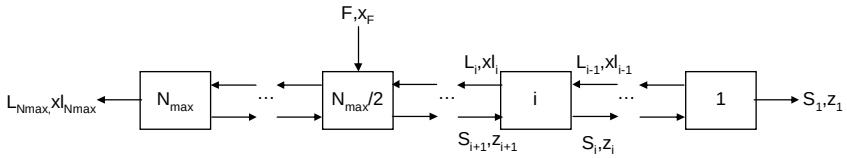

Figure 3: Counter current crystallization cascade

3. Solution Methods for the GDP

Since the number of stages in a crystallization cascade is relatively small, normally $N_{max} \leq 10$, the problem can simply be solved by enumeration rather than applying special complex solution algorithms for GDP if looking at crystallization only. But as already mentioned earlier, for the recovery of more than one pure component layer crystallization has to be combined with other unit operations to form hybrid separation processes. These hybrid processes will contain more than one crystallization unit which results in much higher combinatorics. Thus, enumeration is not a feasible approach if looking at complete flowsheets. In general, two different methodologies are applicable to flowsheet optimization employing shortcut models: a *sequential* or *simultaneous* approach. The sequential solution method ensures first the closure of the mass balance equations of the flowsheet before estimating the economic potential of the process by applying a shortcut method to each unit. In a simultaneous approach the flowsheet mass balances and the shortcut models are solved at the same time. Due to the character of melt crystallization processes, the sequential approach has unfavourable properties. As already stated above, crystallization units comprise only a small number of stages. Consequently the addition or removal of one stage in the process results in a discontinuous alteration of the effluent streams. Therefore, arbitrary product concentrations can not be guaranteed, which means that feasible specifications for the shortcut can not be assured for all solutions of the flowsheet mass balance equations. Consequently, incorporation of a sequential method would result in a costly iterative solution algorithm.

3.1 Branch and Bound

The branch and bound (BB) solution method is sometimes referred to as *implicit* enumeration since a set of NLP subproblems is solved to find the optimal solution of the problem. In comparison to *explicit* enumeration, basically only the search in the discrete decision space is performed in a much more efficient way. A detailed explanation of the method has been reported by e.g. Dakin (1965). Before applying the BB method to the crystallization problem the GDP (5) has to be transformed into a mixed integer nonlinear program (MINLP) utilizing a Big-M reformulation technique.

Table 1: Optimization results for given feed concentration and flow rate and different product specifications.

$z_{1,meta}$ [mol%]	$xl_{N,\,meta}$ [mol%]	N	N_F	Qspec. [kJ/mol]
> 0.99	< 0.6	4	2	302.6
> 0.99	< 0.7	3	1	260.7
> 0.999	< 0.6	5	3	646.2

As a solution algorithm minlpBB by Leyffer and Fletcher from the Tomlab/MINLP module (Holmström et al., 2003) has been employed, with which the results found by explicit enumeration could be reproduced. Some optimization results for the isomeric mixture depicted in Figure 1 are shown exemplarily in Table1.

3.2 Continuous Reformulation of the Discrete-Continuous Problem

Instead of solving the discrete-continuous problem directly, it is also possible to reformulate the MINLP such that no discrete variables are present any more. Thus, only a NLP needs to be solved. Various methods of transforming discrete sets into continuous variables are proposed in the literature (Stein et al., 2004) from which we chose two different approaches: A reformulation employing the Fischer-Burmeister-equation and a transformation based upon a circle equation. The corresponding optimization problems were solved using SNOPT (Gill et al. 1998a) and NPSOL (Gill et al., 1998b). Both approaches for forming purely continuous NLPs from the MINLP did not yield a physically meaningful numerical result for the crystallization problem. Even relaxing the constraints followed by successively approaching the exact continuous reformulations did not improve the results. Therefore, the idea of transforming the MINLP into a NLP does not seem to be applicable to this problem class.

4. Conclusions

A design method for layer crystallization has been presented which allows for the estimation of its profitability at an early design stage, since it is based on feed and product specifications only. It has been shown, that if looking at layer crystallization by itself explicit enumeration is sufficient for solving the GDP. When considering crystallization in the context of the overall process flowsheet a simultaneous approach utilizing a BB method is favourable for the design and optimization of layer crystallization processes.

Acknowledgements

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