Unified Approach for Synthesizing Crystallization-Based Separation Processes

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A procedure for synthesizing crystallization-based separation processes is presented. In an evolutionary manner and without being restricted to a particular crystallization technique, flowsheet alternatives are generated to meet the separation objectives for a given system. This is achieved by recognizing the fact that four basic crystallization-related movements in composition space are sufficient to represent a variety of crystallization processes. Suitable movements are selected based on relevant features of the phase diagram to construct feasible flowsheets. The procedure consists of six steps. First, separation objectives are defined. Second, a separation core structure is generated. Third, the separation sequence and unit operations are selected, followed by adding other units to the structure for proper plant operations. Fifth, appropriate crystallizer type is selected. Finally, economic evaluation and feasibility checks are performed for the generated alternatives. Rules are provided to aid decision-making at each step. The procedure is illustrated with various examples including separation of amino acids, p- and m-cresols, chlorobenzoic acids, calcium carbonate and magnesium oxide from dolomite, and the production of salt.

Introduction

Crystallization has been widely used to separate various organics, inorganics, and biochemicals. The mixture to be separated normally involves a single liquid phase with a number of solutes dissolved in a single solvent. However, the feed can be a mixture of solids (Ng, 1991). Also, rather than having a single liquid phase, the system can involve a gas phase (Jagadesh et al., 1992) and two or more liquid phases (Berry et al., 1997). With the additional complexities in solid-liquid phase behavior such as the presence of eutectics and compound formation, and the possibility of reaction among the components in the system, it is not surprising that a wide variety of crystallization-based separation techniques have been invented.

In *fractional crystallization*, operations such as heating/cooling, solvent addition/removal are used to recover two or more of the solutes from a multicomponent solution (Fitch, 1970; Cisternas and Rudd, 1993; Cisternas and Swaney, 1998, Thomsen et al., 1998; Cisternas, 1999). Instead of the solute, if the solvent is recovered by cooling, the process is referred to as *freeze crystallization* (Mullin, 1993). In *extractive crystallization*, an extraneous solvent is added to assist the separation of a multicomponent mixture (Findlay and Weedman, 1958; Dye and Ng, 1995a); only cooling crystallizers are used in such processes. A more general technique is the addition of an extraneous component, which may be a gas, a liquid, a supercritical fluid, or a solid, to effect separations (Hanson and Lynn, 1989; Weingaertner et al., 1991; Liu and Nagahama, 1996) and is referred to as *salting-out, drowning-out, solventing-out*, or *dilution crystallization.* The use of a hydrotrope, which significantly affects the solubility of one or more of the solutes, also falls into this category (Colônia et al., 1998). In *adductive crystallization*, the added component reacts with one of the components to form an adduct which can easily be separated from the mixture (Dale, 1981). Finally, solid crystals can be produced as the result of a chemical reaction between the components. This technique is known as *reactive crystallization* (Berry and Ng, 1997). In *dissociation extractive crystallization*, an aqueous solution containing a neutralizing agent and an organic solvent are simultaneously added to a mixture to effect preferential precipitation of one of the organic bases in the form of a complex (Gaikar and Sharma, 1987; Gaikar et al., 1989).

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For some of these techniques, step-by-step procedures to construct flowsheet alternatives are not available. This is a serious omission because significant advantages can be gained with a superior and timely process design. While, for other techniques, ready-made process alternatives have been formulated to handle identified phase behaviors (Rajagopal et al., 1991; Dye and Ng, 1995b; Berry and Ng, 1996; Berry et al., 1997), the use of a combination of the different techniques discussed above to further enhance process performance was not considered. Furthermore, complete separation of all solutes was always assumed.

In this article, we present a unified synthesis procedure to generate in an evolutionary manner flowsheet alternatives for crystallization-based separation processes. The procedure is not limited to a specific crystallization technique and can be applied to both nonreactive and reactive systems. While the procedure is applicable for the separation of mixtures containing any number of components, the discussion is limited to a quaternary system (three solutes and a solvent) to maintain clarity of the presentation.

The present approach is akin to the process boundary approach for separations synthesis (Berry, 1997; O'Young et al., 1997; Safrit and Westerberg, 1997; Ahmad et al., 1998; Rooks et al., 1998; Pressly and Ng, 1999). The composition space of a given system can be partitioned into different regions by equipment limitations or thermodynamic boundaries. The aim is to purposefully maneuver to the proper region(s) to produce the desired product(s) and to purge impurity byproducts. This is achieved by configuring the processing units in such a way that, whenever necessary, the limitation or boundary of one unit is bypassed with a suitable movement. In other words, every unit involved in the process is represented in composition space as a transition from the feed composition point(s) to the product composition point(s) of the corresponding unit. We begin with an identification of the basic movements for crystallization-based separation processes.

Basic Movements in Composition Space

In principle, there are only two basic operations in crystallization-based separation processes: temperature swing and composition swing. Pressure swing is not considered because normally pressure has little effect on solid-liquid equilibrium. Composition swing can be achieved in three different ways. Thus, it is convenient to define four basic movements in composition space as follows: (1) heating or cooling, (2) stream combination or splitting, (3) solvent addition or removal, and (4) addition or removal of a mass separating agent (MSA). An MSA is defined as any component not initially present in the feed and can be a gas, liquid, or solid. These movements are illustrated below using phase diagrams for ternary and quaternary systems. Readers unfamiliar with such diagrams are referred to Dye and Ng (1995a,b) and Berry et al. (1997) for additional details. Table 1 provides a list of the equipment units for executing the basic movements. Sometimes, several movements can be performed in a single equipment unit. For example, both cooling and solvent removal can be performed in an evaporative crystallizer.

Figure 1a shows the temperature-composition diagram for a ternary system, its polythermal projection, and two isothermal cuts at T_h and T_c. Salient features of the polythermal projection are depicted in Figure 1b. The lines *AB-ABS*, *AS-ABS*, and *BS-ABS* are the *eutectic troughs*, along which a solution is saturated with two components. These lines divide the triangle into three *compartments: A*, *B*, and *S*, and also serve as boundaries between the compartments. A compartment is the subspace in a polythermal projection within which a component can be crystallized in pure form. Figure 1c shows two isothermal cuts superimposed on top of each other. The *saturation region* (two of which are shaded) indicates the region where a pure component solid is in equilibrium with a liquid solution. A saturation region is part of the compartment of the same species, as seen in an isothermal cut. Figure 1a shows that point *1* (an unsaturated solution) moves to point *2* (a saturated solution) by *cooling*. In the projections, these two points coincide. Upon further cooling to temperature T_h, the solution enters the saturation region of *B*, as can be seen in Figure 1c. Consequently, pure *B* crystallizes out of the solution, and the composition of the solution moves along the solubility surface to point *3* (Figure 1a). *Solvent addition* then moves the composition towards *S*, across the boundary between compartments *A* and *B*, to point *3′* (Figure 1b). When this solution is cooled to temperature T_c, crystals of pure *A* are formed and the composition moves to point *4*. *Heating* raises point *4* to *4′*, and *stream combination* of points *4′* and *5* yields point *1*, which is back in compartment *B*.

Figures 2a and 2b are the polythermal projection and the isothermal cuts, respectively, of a three-solute system containing one solvent. Their Jänecke projections are shown as insets. In the polythermal projection of a typical simple-

Table 1. Basic Operations of Crystallization-Based Separation Processes

Operation	Equipment Units	Representation in Composition Space
Cooling/heating	Crystallizer, heat exchanger	Movement along the temperature axis
Stream combination	Mixer	Joining the original points by a straight line
Stream split	Evaporator, distillation column, decanter, extractor	Movement along a straight line from the original point in opposite directions
Solvent addition	Crystallizer, mixer/dilution tank	Movement along a straight line towards the apex representing the solvent
Solvent removal	Crystallizer, distillation column, evaporator	Movement along a straight line away from the apex representing the solvent
MSA addition	Crystallizer, mixer/dilution tank	Movement along a straight line towards the apex representing the MSA
MSA removal	Crystallizer, distillation column, evaporator, adsorption column	Movement along a straight line away from the apex representing the MSA

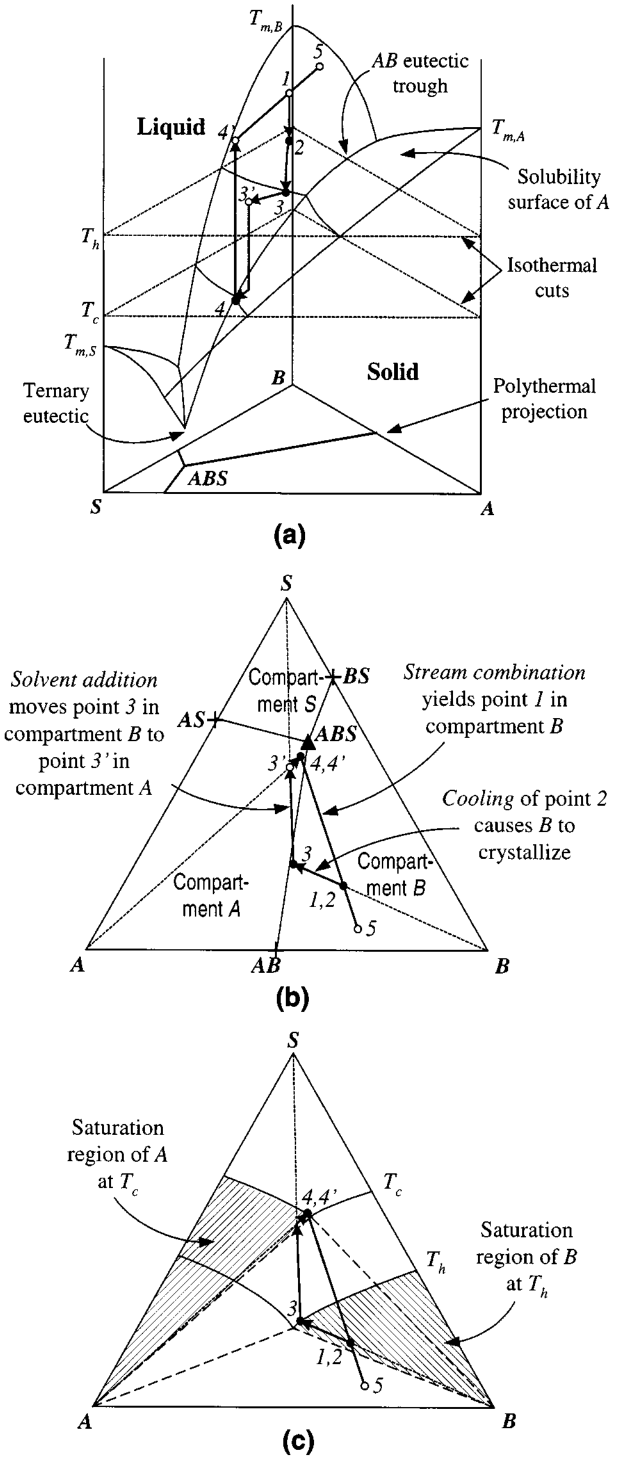


Figure 1. Isobaric phase diagrams for a simple eutectic two-solute system: (a) temperature-composition diagram, (b) polythermal projection, (c) isothermal cuts at T_h and T_c.

○ = unsaturated, ● = saturated.

eutectic system (Figure 2a), there are six binary, four ternary, and one quaternary eutectics. There are six *eutectic surfaces*, dividing the terahedron into four compartments: *A*, *B*, *C*, and *S*. In the isothermal phase diagram, the projection of the saturation region of *A* at T_2 is indicated by the shaded region (Figure 2b inset). Stream combination of point *6*, which is located in compartment *C*, with point *7* yields point *8*, which is in compartment *B*. *Solvent removal* moves point *8* across the boundary between compartments *A* and *B* to point *8'*. Note that it is necessary that point *8* lies on the Jänecke projection of the eutectic surface *AB-ABC-ABCS-ABS* (see Figure 2a inset); otherwise, solvent addition or removal would not result in the desired compartment crossing. The combination of cooling to temperature T_2 and solvent removal causes *A* to crystallize out and point *8* to move to point *9*.

The addition of MSAs increases the number of components in the system, and, thus, the complexity of the system. For a two-solute system with one solvent, the addition of an MSA leads to a quaternary system, and the phase diagram can be represented in the same way as depicted in Figure 2. However, for systems with three or more solutes, representation of the polythermal projection and isothermal cuts in 3D is no longer possible. Such high-dimensional systems can be represented using cuts of the phase diagram, taken at different levels of MSA concentration. These cuts are sometimes referred to as isoplethal cuts (Colônia et al., 1998). Figure 3 depicts two isoplethal cuts (0% and 5% *D*) of the Jänecke projections of the polythermal phase diagrams for a three-solute (*A*, *B*, *C*) system. In such a diagram, one can only see

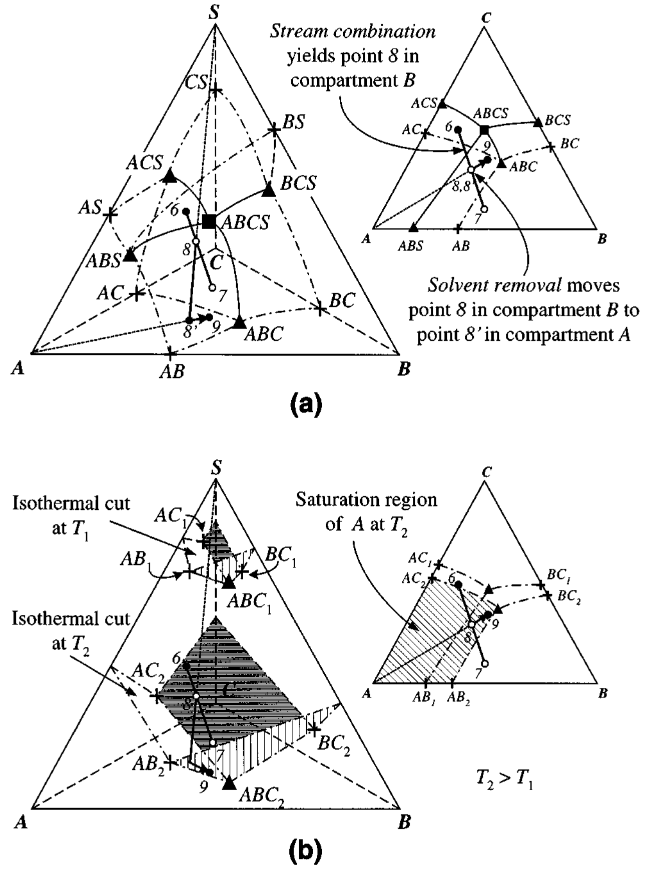


Figure 2. Isobaric phase diagrams for a simple eutectic three-solute system:

(a) Polythermal projection; (b) isothermal cuts at T_1 and T_2.

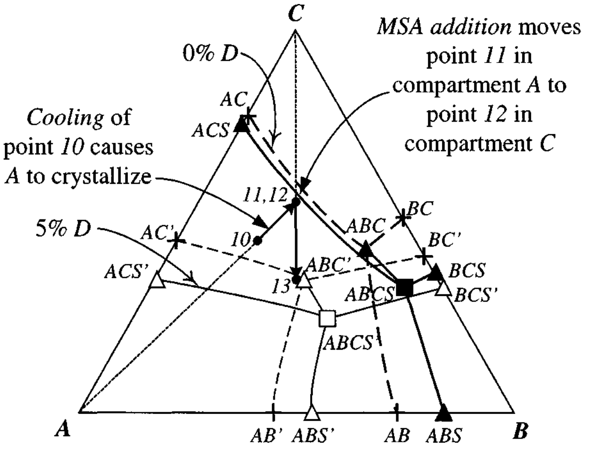


Figure 3. Isoplethal cuts of the Jänecke projection of the polythermal phase diagram for a three-solute, one solvent system with an MSA.

the cuts of compartments *A*, *B*, and *C*. For example, the cut at 0% *D* of compartment *A* is bounded by the eutectic surfaces *AB-ABS-ABCS-ABC* and *AC-ACS-ABCS-ABC*, while the cut at 5% *D* of the same compartment is bounded by the eutectic surfaces *AB′-ABS′-ABCS′-ABC′* and *AC′-ACS′-ABCS′-ABC′*. Point *10* represents a solution containing *A*, *B*, *C*, and *S*, thus lying on the 0% *D* cut. Since this point is in compartment *A*, cooling leads to crystallization of *A*. The solution composition moves to point *11*. *MSA addition* moves point *11* to point *12*, which is located on the 5% *D* cut. Despite the movement in the high-dimensional composition space, both points are represented by the same circle in this projection, because the proportions of *A*, *B*, and *C* in the solution remain the same. However, point *12* is now in compartment *C*, whose cut at 5% *D* is bounded by the eutectic surfaces *AC′-ABC′-ABCS′-ACS′* and *BC′-ABC′-ABCS′-BCS′*. Cooling of point *12* results in the crystallization of *C*, and the composition moves to point *13*.

Unified Synthesis Procedure

Crystallization-based separation processes can be classified into two groups. Processes in the first group do not use an MSA, while those in the second group do. As will be explained later, the use of an MSA is advantageous or even essential for systems with heat-sensitive components, high boiling point rise, high heat of vaporization, solubility insensitivity to changes in temperature, or a feed made up of solids with high melting points.

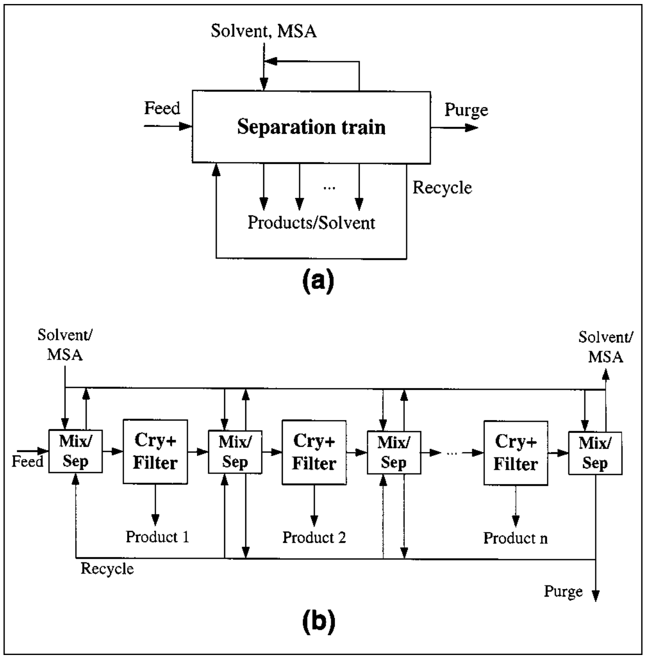


Figure 4. Generic structure of crystallization-based separation proceses.

(a) Input-output structure; (b) recycle structure.

Whether an MSA is involved or not, we should collect input information, including the feed phase and composition, the number of components, and the number of reactions in the system (if any). Experimental data and/or parameters required in solid-liquid phase equilibrium calculations for constructing phase diagrams are essential. It is also often useful to have information on vapor-liquid and liquid-liquid equilibrium. The strategy is to construct flowsheet alternatives by identifying the necessary movements in composition space based on the features of the phase diagram.

Figure 4a depicts the input-output structure of a crystallization-based separation process. The box represents the separation train consisting of one or more crystallizers. We may need to add or remove solvent or MSA at appropriate locations. Recycle and purge streams may be present. This structure can be expanded to give a recycle structure as depicted in Figure 4b. Each crystallizer followed by a filter is used to recover a solids product. A mixer or a separator is placed between each crystallizer/filter to allow solvent or MSA addition or removal, and stream combination or splitting.

Table 2. Movements and Relevant Features in a Phase Diagram for Achieving a Desired Objective

		Features to Look for in	
Objective	Movements to Use	Two-Solute System	Three-Solute System
Moving from one compartment to another	Solvent addition or removal, MSA addition or removal, stream combination or split	Eutectic troughs in the polythermal phase diagram	Eutectic surfaces in the polythermal phase diagram
Effecting precipitation of a solid product	Cooling or heating, solvent addition or removal, MSA addition or removal*	Single saturation curve in the isothermal cut	Single saturation surface in the tetrahedron isothermal cut

*Remark: Stream combination or split is not used here because we normally do not create supersaturation with this movement.

Table 3. Steps for Generating Flowsheet Configurations of Crystallization-Based Separation Processes

Step 1. Definition of separation objectives and construction of phase diagrams
Step 2. Construction of separation core structure
Step 3. Selection of separation sequence and unit operations for crossing separation boundaries
Step 4. Addition of unit operations for proper plant operations
Step 5. Selection of crystallizer type
Step 6. Evaluation of flowsheet alternatives

Table 4. Classification of Components in the Feed to Crystallization-Based Separation Processes

Class of Components	Objectives
Feed reactor effluent stream or feed to a reactive crystallizer	
· Desired product	Recover as pure solids
· Unconverted reactant	Purge or recycle to reactor as liquid
· Byproduct	Purge as liquid or recover as solids
· Solvent	Recycle as liquid
Feed: solution or solid mixture from natural sources	
· Desired product	Recover as pure solids
· Soluble impurities	Purge as liquid or recover as solids
· Insoluble impurities	Purge as solids

Table 5. Input Information for Separating Three Solutes (Example 1)

Feed Composition (mole fraction)	
A	0.35
B	0.05
C	0.10
S	0.50
Pure Component Melting Point (°C)	
A	59.7
B	44.2
C	75.9
S	−43.2
Binary Eutectic Temp. (°C)	
AB	15.8
AC	22.4
BC	3.4
AS	−52.7
BS	−46.6
CS	−52.3
Ternary Eutectic Temp. (°C)	
ABC	−7.7
ABS	−58.8
ACS	−54.3
BCS	−54.7
Quaternary Eutectic Temp. (°C)	
ABCS	−60.2
Boiling Point at 1 atm (°C)	
A	214.4
B	208.4
C	209.1
S	−2.1

The movements in the composition space have two objectives. The first is to move from one compartment to another, preferentially a contiguous one, in order to produce a desired product at that compartment. This is accomplished in the mixers or separators depicted in Figure 4b. The second objective is to effect precipitation of the desired product in the crystallizer after getting into its compartment. Table 2 summarizes the movements to use and the features of the phase diagram to look for to achieve each goal. To select the movements for crossing into another compartment, we need to locate the compartment boundaries. The use of a polythermal phase diagram (Figures 1b and 2a) is preferred, because the boundaries are more evident. Alternatively, we can use a series of isothermal cuts taken over the practical temperature range to represent the phase behavior, which in some cases may be more convenient. This is especially so when reaction or liquid-liquid immiscibility is involved. Saturation regions at the different cuts can be compared to locate the boundaries in polythermal projections. For example, eutectic trough *AB-ABS* in Figure 1b can be reconstructed in Figure 1c by connecting the double saturation points at different temperatures. Similarly, the eutectic surface *AB-ABC-ABCS-ABS* in Figure 2a can be reconstructed in Figure 2b by combining the *AB-ABC* double saturation curves at different temperatures. To effect precipitation, we may have to change temperature, remove solvent, or add MSA, in order to reach the single saturation surface of the crystallizing component.

The strategy is implemented in a six-step procedure listed in Table 3. Steps 1 to 5 are discussed below for generating flowsheet alternatives without and with MSA. Step 6 deals with the evaluation of the alternatives using material balance and economic analysis in order to determine the best flowsheet. This step will be discussed in a separate section with a specific example−the production of salt.

Flowsheet alternatives without using MSA

To make it easier to understand the decision-making process in each step, the procedure will be described alongside Example 1. It involves a liquid-phase reaction which proceeds to complete conversion in solvent *S*. The main product of this reaction is *A*, and *B* and *C* are byproducts, which can be used as raw materials for other processes. It is desired to obtain all three components from the solution as pure solids.

Step 1: Definition of Separation Objectives and Construction of Phase Diagrams. The feed to a crystallization-based separation process can be a mixture from natural sources such as mineral ores or seawater, a mixture in a reactor effluent, or a feed stream of reactants to a reactive crystallizer. It is convenient to classify the components as shown in Table 4, which also lists some possible separation objectives for each class of components. Solvents are those components that are not recovered as solids. They usually have much lower melting points compared to the other components. The desired products, byproducts, soluble impurities, and unconverted reactants are referred to as solutes. After defining the objective, an appropriate phase diagram is constructed based on the input information.

Step 1 for Example 1: Four components (three solutes and one solvent) are involved in this system, and the objective is to separate all three solutes. Table 5 shows the input parameters. It is also given that the solubility of all components increases with increasing temperature. Figure 5a depicts the polythermal phase diagram for the system with the feed represented by point F.

Step 2: Construction of Separation Core Structure. In this step, we construct the core structure of the separation train, consisting of a series of crystallizers and filters. Rules to guide decision-making are given in Table 6.

First, the required number of crystallizers needs to be determined based on the objective of separation. Since each desired product should be crystallized separately, the minimum number of crystallizers in the core structure is equal to the number of desired products. At this stage, it is assumed that only cooling crystallizers are used; this will be relaxed in Step 5. The recycle stream usually contains byproducts and soluble impurities, and partial purging is necessary to avoid accumulation of these components. The fraction of final mother liquor to be purged is dictated by the maximum allowable concentration of impurities in the mother liquor (Cesar and Ng, 1999). Depending on the phase behavior,

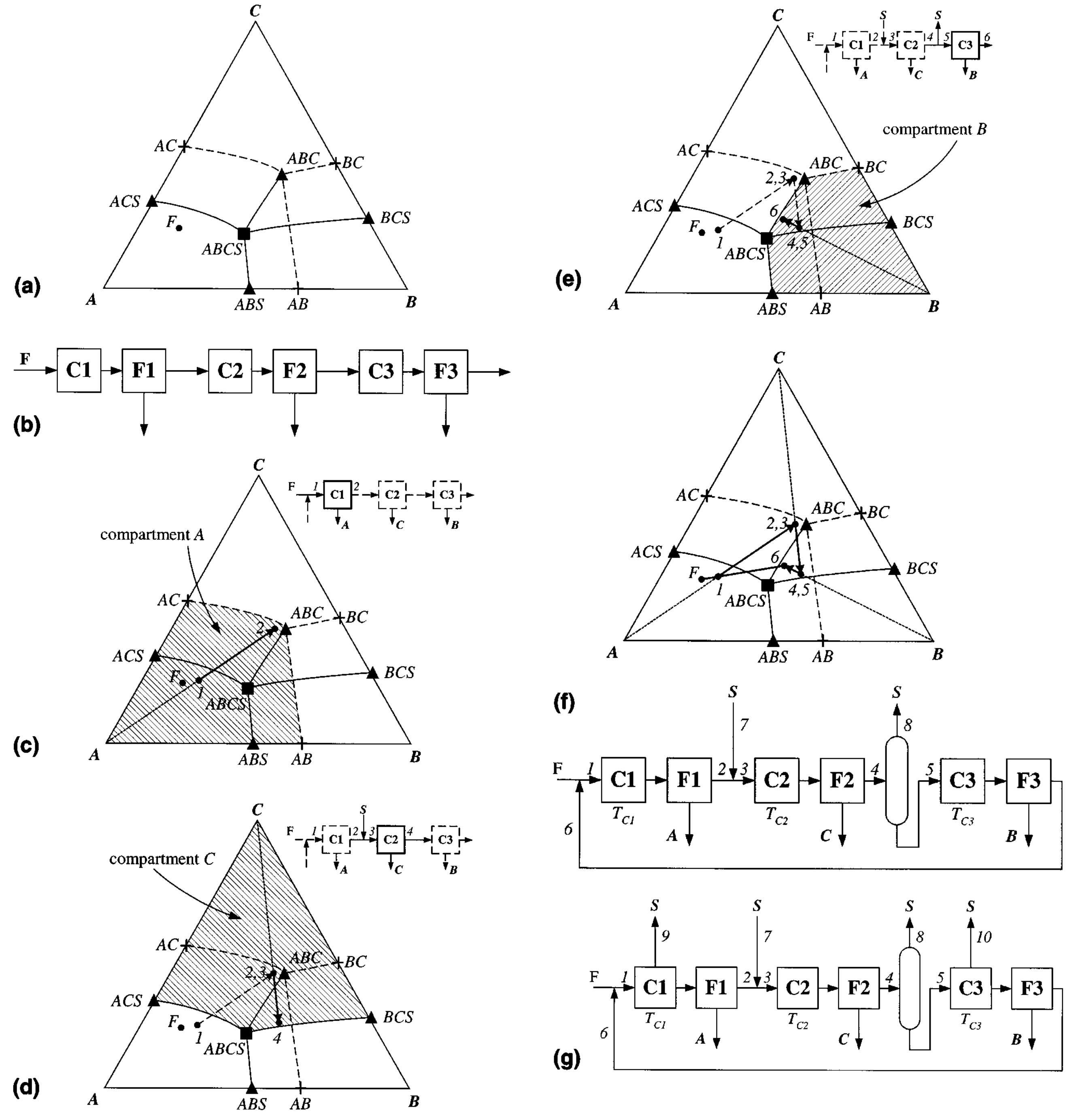


Figure 5. Development of flowsheet alternatives for Example 1.

(a) Jänecke projection of the polythermal phase diagram; (b) core separation structure; (c) separating *A* in the first crystallizer; (d) separating *C* in the second crystallizer; (e) separating *B* in the third crystallizer; (f) flowsheet structure at Step 3; (g) alternative of using evaporative crystallizers.

Table 6. Rules for Generating Flowsheet Configurations without Using MSA

Rules for Constructing Separation Core Structure	
Rule 1.	Use a crystallizer for recovering each desired product.
Rule 2.	Use only one crystallizer to recover components that do not need to be obtained in a pure form, if their compartments share a boundary.
Rule 3.	Use partial purging of the final mother liquor, if complete recovery of all solutes is impossible or undesirable.
Rules for Selecting Separation Sequence and Unit Operations	
Rule 4.	If the feed is located in the compartment of a desirable solute, separate that particular component first.
Rule 5.	Choose the order of separation by considering possible moves to a contiguous compartment.
Rule 6.	If it is not possible to obtain a desired product by crossing into a contiguous compartment, consider crystallizing an intermediate component.
Rule 7.	Use solvent addition or solvent removal to cross from one compartment to another, whenever possible.
Rule 8.	Consider using addition of reactant, removal of volatile product, or changing inert concentration to cross the compartment boundaries in reactive systems.
Rule 9.	Consider stream combination to cross from one compartment to another, if and only if every component entering the recycle loop thus formed has an exit point.
Rules for Selecting Additional Units for Proper Plant Operations	
Rule 10.	If the feed is located in the solvent compartment, add a solvent removal unit at the beginning of the separation train.
Rule 11.	Add a solvent removal unit after the last crystallizer, if the solvent enters through the feed or at any point along the process train, while there is no natural exit for the solvent.
Rules for Choosing Crystallizer Type and Operating Condition	
Rule 12.	Operate a crystallizer at a temperature where high yield can be obtained, unless there are other constraints.
Rule 13.	If solvent addition (removal) is used to move into the compartment of the crystallizing component, operate the crystallizer at a temperature where the solubility of the crystallizing component is lower (higher) compared to that in the preceding crystallizer.
Rule 14.	Do not use an evaporative crystallizer if the boiling point of the solvent is substantially higher than the melting point of the crystallizing component.
Rule 15.	Consider using an evaporative crystallizer if the melting point of the crystallizing component is much higher than the desired crystallization temperature or if the solvent has a high relative volatility, while there is no solvent addition unit immediately prior to the crystallizer.

purging can lead to a significant product loss. Such a situation can be avoided by recovering the byproducts or impurities in an additional crystallizer. Several components can be co-crystallized in the crystallizer, since there is no need to obtain byproducts or impurities as pure components. Similarly, unconverted reactants can also be recycled or crystallized. The difference is that recycling these components to the reactor can lead to a complete conversion, and purging would not be necessary to avoid accumulation.

Step 2 for Example 1: For this system, we need three crystallizers (Rule 1). Since all solutes are recovered as solids, a purge stream is not necessary (Rule 3). The preliminary flowsheet structure is depicted in Figure 5b.

Step 3: Selection of Separation Sequence and Unit Operations. Rules for this step are also presented in Table 6. We note that every compartment associated with a desirable product should be visited at least once. The separation sequence consists of a series of compartments that can be visited by crossing the boundary or boundaries among them. There may be several possible separation sequences, which should all be considered as process alternatives. It is possible that after arriving at a particular compartment, all contiguous compartments do not produce a desired product. In order to proceed further in the composition space, we can crystallize an intermediate product from one of the contiguous compartments. Examples of such a component include compounds, adducts, or even a solvent.

Each movement in the sequence must be selected by observing the phase behavior of the system on hand. For example, for the system depicted in Figure 1b, it is possible to use solvent addition to move point *3* in compartment *B* to point *3′* in compartment *A*, because of the inclination of the *AB* eutectic trough (line *AB*-*ABS*). Similarly, as depicted in the inset of Figure 2a, the inclination of the eutectic surface *AB*-*ABC*-*ABCS*-*ABS* suggests that solvent removal should be used to move from compartment *B* to *A*. Solvent addition or removal is the preferred way to cross boundaries between compartments, because we can choose a low boiler for easy recovery. There are cases, however, where the phase behavior does not allow this. For example, if the position of line *AB*-*ABS* in Figure 1b were such that points *S*, *ABS*, and *AB* are collinear, solvent addition or removal would not have caused a compartment crossing. In the inset of Figure 2a, the same situation is observed if line *AB*-*ABC* coincides with line *ABS*-*ABCS*. For these cases, we must consider other options such as using stream combination or crystallizing an intermediate component. For reactive systems, we can also consider addition of reactants and removal of products. If none works, an MSA must be used.

To determine the feasibility of a separation sequence, the corresponding process path is drawn on the phase diagram. In order to have a valid process path, each point must lie on the appropriate region. There are three conditions that must be satisfied by the feed and product of a crystallizer in the sequence: the feed must be in the compartment of the crystallizing component; the output must be transferable to the compartment of the next component to be crystallized; the feed, the output, and the apex representing the crystallizing component must be collinear.

When considering stream combination as an alternative to solvent addition and removal, care should be taken to avoid creating an infeasible flowsheet. For example, stream combi-

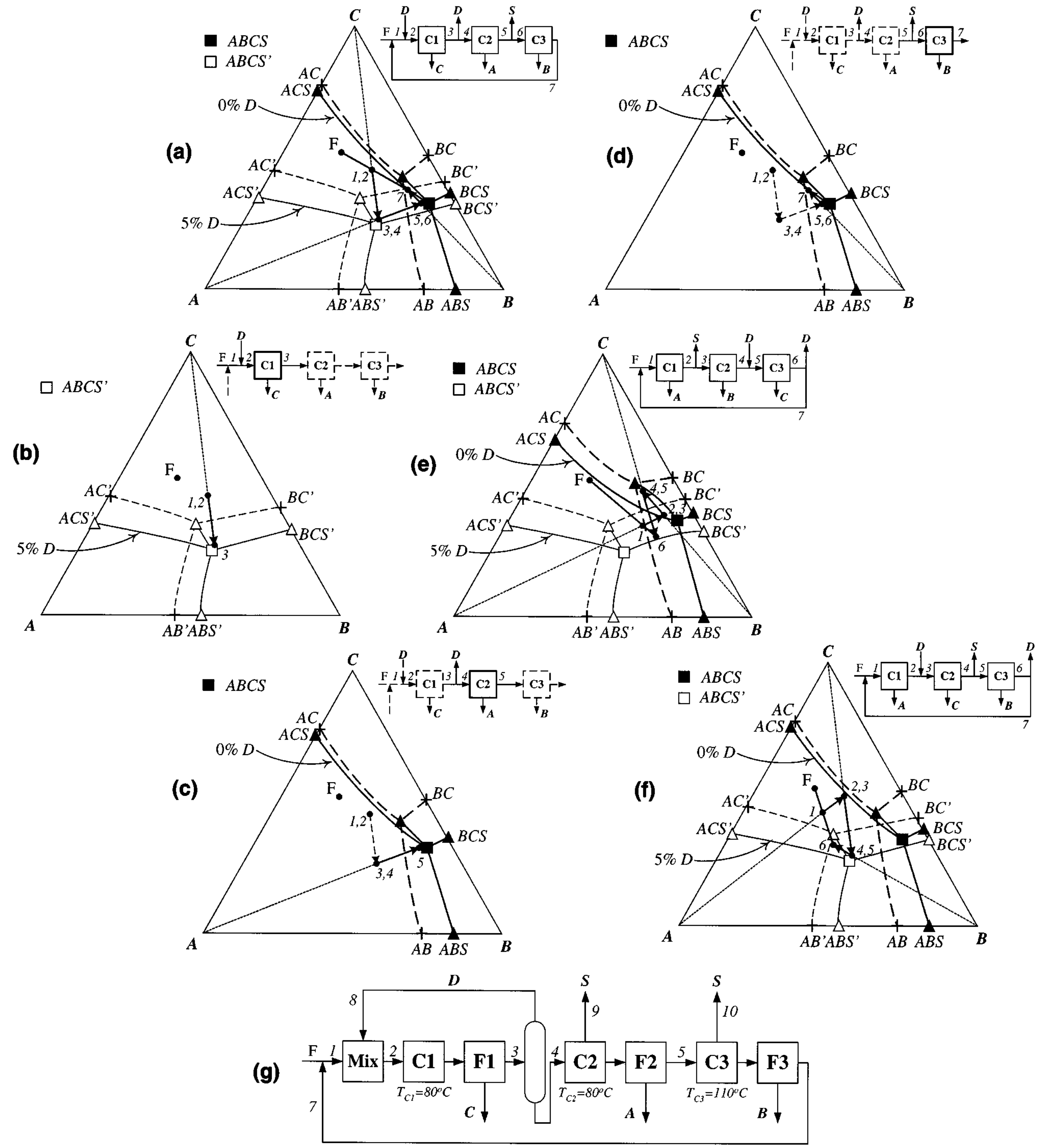


Figure 6. Development of flowsheet alternatives for separating an organic and two amino acids (Example 2).

(a) *C-A-B* alternative; (b) separating *C* in the first crystallizer; (c) separating *A* in the second crystallizer; (d) separating *B* in the third crystallizer; (e) *A-B-C* alternative; (f) *A-C-B* alternative; (g) final flowsheet.

nation tends to lead to a recycle stream which always creates a closed loop. It is important to make sure that each component in the system has an exit point from the loop.

Step 3 for Example 1. Since the feed is located in compartment *A*, component *A* should be separated first (Rule 4). The next component to be crystallized can be either *B* or *C* (Rule 5). In this example we discuss the option to separate *C* next and crystallize *B* in the third crystallizer. The flowsheet development at this step is shown alongside the construction of process paths in Figures 5c–5e. The process paths are constructed by taking into account the three conditions discussed previously. Point *1*, which is the feed to the first crystallizer (C1), must be in compartment *A* (Figure 5c). The output of this crystallizer, point *2*, must lie on the projection of the eutectic surface *AC-ABC-ABCS-ACS*, such that it is transferable to compartment *C*. Points *A*, *1*, and *2* must be collinear. Next, we separate *C* in the second crystallizer (Figure 5d). Line *ACS-ABCS* appears closer to *A* compared to *AC-ABC*, indicating that solvent addition can be used to move from compartment *A* to *C* (Rule 7). Point *4* must lie on the projection of eutectic surface *AB-ABC-ABCS-ABS*, and points *C*, *3*, and *4* must be collinear. After crystallizing *C*, we need to cross the eutectic surface *BC-ABC-ABCS-BCS* to reach compartment *B* (Figure 5e). In order to accomplish this task, we use solvent removal between the second and third crystallizers (Rule 7). The final mother liquor (stream 6) is then recycled to the feed, as suggested by the recycle structure (Figure 4b). The final flowsheet is shown in Figure 5f, along with all process paths drawn on top of the phase diagram.

Let us now consider the option of using stream combination. Observation of the phase diagram reveals the possibility of combining the final mother liquor (stream 6, located in compartment *B*), with stream 2 (located in compartment *A*) to cross the boundary between compartments *A* and *C*. Unfortunately, this will create a loop where there is no exit point for *A*, which enters the loop through stream 2 (Rule 9). For this reason, regrettably, the options reported by Dye and Ng (1995a) as Figures 9 and 10 are actually infeasible.

Step 4: Addition of Unit Operations for Proper Plant Operations. In Step 4, we identify the need for additional treatments to the feed, final mother liquor, and purge stream. If the feed composition lies in the solvent compartment, a solvent removal unit should be added because no solute can be crystallized from this solution using cooling only. Other unit operations are added to ensure that there would be neither solvent accumulation nor depletion in the system, and to minimize product loss.

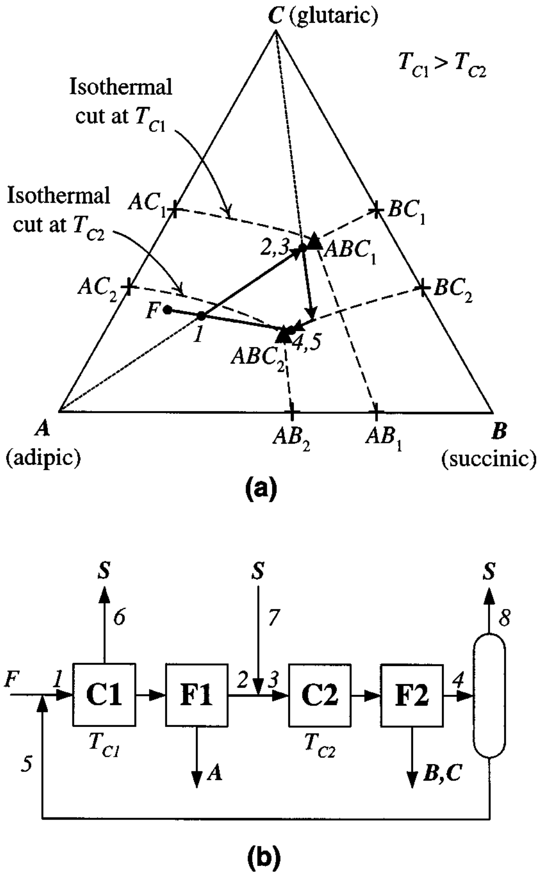
Step 4 for Example 1: In this process, we do not need to add a solvent removal unit since we already have solvent removal before the third crystallizer (Rule 11). Therefore, no further modification is made to the flowsheet in Figure 5f. The alternative depicted in Figure 5f actually conforms to a conventional extractive crystallization separation scheme, referred to as type IIa in Dye and Ng (1995a).

Step 5: Selection of Crystallizer Type. The alternative of solvent removal from the crystallizer either by evaporation or vacuum is considered in Step 5. First, we choose the crystallizer operating temperature by considering two constraints. The first constraint is the fact that when solvent addition or removal is used to cross a compartment boundary, the two adjacent crystallizers must be operated at different temperatures. To clarify this point, let us consider the phase behavior depicted in Figure 1a. After adding solvent to cross from compartment *B* to *A*, the solution temperature (point *3′*) must be lowered before *A* can crystallize. Similarly, if solvent removal were to be used to move point *4* to compartment *B* (Figure 1b), the point must first be raised to a temperature at which the solution becomes unsaturated (point *4′*); otherwise, *A* will co-crystallize and pure *B* cannot be obtained.

The second constraint is the range of crystallizer operating temperatures, which is governed by many factors. A useful observation of the phase diagram is obtained by examining the relative position of a crystallizer outlet composition to a eutectic. In typical solid-liquid equilibrium behavior, the higher-order eutectics have lower temperatures. For example, in a ternary system, the ternary eutectic temperature is lower than those of the binary eutectics. Therefore, the closer the crystallizer output is to the ternary eutectic, the lower its operating temperature can be. However, it cannot be lower than the eutectic temperature. In reality, the lower temperature limit is usually governed by the high energy cost for refrigeration. It is generally preferable to keep the crystallizer temperature above 0°C (Barnicki and Siirola, 1997), although direct cooling by injection of a liquefied inert gas (such as nitrogen) can be used to achieve very low temperatures. The upper limit is influenced by factors such as boiling point of the solvent, decomposition temperature of a component, and availability of steam for heating, among others. Rajagopal et al. (1991) pointed out that for typical solid-liquid behavior, we have the following constraint for the temperature of the crystallizer used to separate component *A*

$$T_C < T_{m,A} \qquad (1)$$

If we use an evaporative crystallizer, the solvent must evaporate at T_C. Therefore, the bubble point of the solution, $T_{b,S}'$ (°C), which is the boiling point of pure solvent plus the eleva-



(a)

(b)

Figure 7. Phase behavior and flowsheet structure of a system mimicking adipic, glutaric, and succinic acids (Example 3).

tion due to the presence of solutes, must obey the constraint

$$T_{b,S}' < T_{m,A} \tag{2}$$

In practice, $T_{b,S}'$ can be lowered by reducing the pressure. However, if the normal boiling point of the solvent is substantially higher than $T_{m,A}$, very low pressure is needed to obey the constraint in Eq. 2, so that the use of an evaporative crystallizer may not be feasible. Generally, a vacuum level lower than 7 kPa requires a complicated system (Barnicki and Siirola, 1997). For reactive crystallization, reaction equilibrium may dictate the operating temperature.

Second, we consider the sensitivity of solubility to changes in temperature. For an ideal system, in which $\gamma_i = 1$, the solubility change with respect to temperature evaluated at T_C is

$$\left.\frac{dx_i}{dT}\right|_{T=T_C} = \frac{\Delta H_{m,i}}{RT_C^2} \exp\left[\frac{\Delta H_{m,i}}{R}\left(\frac{1}{T_{m,i}} - \frac{1}{T_C}\right)\right]. \tag{3}$$

If

$$\frac{\Delta H_{m,i}}{RT_C} > 2, \tag{4}$$

which is true for many real systems (Perry et al., 1997), and the crystallizer temperature is much lower than the melting point of the crystallizing component, the value of dx_i/dT tends to be small. In other words, the solubility of the crystallizing component does not vary significantly with temperature. In such a case, an evaporative crystallizer is an attractive option. However, if a solvent addition unit has just been used to cross a eutectic surface, there is no advantage in using an evaporative crystallizer.

Step 5 for Example 1: Since solvent addition is used between C1 and C2, and *C* is less soluble at a lower temperature, we must operate C2 at $T_{C2} < T_{C1}$ (Rule 13). Similarly, we have $T_{C3} > T_{C2}$. Assuming typical behavior, T_{C2} cannot be lower than the *ABCS* eutectic temperature. It is desirable to have T_{C1} and T_{C3} as low as possible (Rule 12). This means the crystallizers must be operated with refrigeration. The optimum temperatures can be found by considering the overall process economics (Rajagopal et al., 1991). We now look at the possibility of using evaporative crystallizers. Since no solvent addition unit is present prior to the third crystallizer, which is used to recover *B*, and the boiling point of solvent (-2.1°C) is much lower than the melting point of *B* (44.2°C), an evaporative crystallizer can be used for C3 (Rules 14 and 15). For a similar reason, there is an incentive to use an evaporative type for the first crystallizer as well. The final flowsheet is shown in Figure 5g.

It can be shown that this procedure leads the user to rediscover all fractional and extractive crystallization alternatives discussed by Dye and Ng (1995a, b). In addition, it also guides

Table 7. Additional Rules for Generating Flowsheet Configurations Using MSA

Rules for Selection of MSA	
Rule 16.	Consider using an MSA (class I or II) that selectively reduces the relative solubilities of the desired products, if it is desired to crystallize a component with high solubility or if solvent addition/removal cannot be used to cross a compartment boundary.
Rule 17.	Consider using a class I MSA to change the solubility of a desired product that changes only slightly with temperature.
Rule 18.	Consider using a class II MSA, if the feed contains materials having a narrow temperature range to which they can be exposed (heat-sensitive).
Rule 19.	Consider using a class III MSA, if one of the components in the feed can form a product which has a low solubility in the solution.
Rule 20.	Consider using a class IV MSA, if the feed is a mixture of solids or it is a binary mixture separated by a eutectic.
Rule for Constructing Separation Core Structure	
Rule 21.	Consider total purging of the final mother liquor, if recycling does not change the composition of this stream.
Rules for Selecting Separation Sequence and Unit Operations	
Rule 22.	Add the MSA at the beginning of the section where it is utilized.
Rule 23.	Use an MSA addition (removal) unit after a crystallizer to cross a compartment boundary, if the crystallizer output stream would move to the destination compartment at a higher (lower) concentration of MSA.
Rule 24.	Recycle MSA-rich stream to an upstream MSA addition unit.
Rule 25.	If the feed is a solid mixture, consider recovering soluble impurities using selective dissolution and crystallization (Ng, 1991).
Rules forSelecting Additional Units for Proper Plant Operations	
Rule 26.	If the solvent-rich stream to be sent to the next stage or to be partially purged still contains MSA, consider using an additional separation unit to recover the MSA from this stream.
Rule 27.	If there is no exit for the solvent, and an MSA-rich stream to be recycled still contains solvent, consider removing solvent from this stream.
Rule 28.	If insoluble impurities are present in a solid feed, separate them using a filtration unit immediately after the dissolver.
Rule 29.	Add a separation unit to decompose any crystallized intermediate product. If it is not decomposable, send it to an upstream dissolver or to another separation system.
Rules for Choosing Crystallization Type	
Rule 30.	Do not use an evaporative crystallizer if the MSA is more volatile or just slightly less volatile than the solvent.
Rule 31.	Consider feeding the MSA-rich stream directly into the crystallizer.

Table 8. Input Information for Separating an Organic and Two Amino Acids (Example 2)

Feed Composition (mol fraction)	
A (organic acid)	0.20
B (amino acid)	0.10
C (amino acid)	0.30
S (water)	0.40
Pure Component Melting Point (°C)	
A	151
B	295
C	287
D	−50
S	0.0
Binary Eutectic Temp. (°C)	
AB	118.2
AC	115.6
BC	195.5
Ternary Eutectic Temp. (°C)	
ABC	72.1
Quaternary Eutectic Temp. (°C)	
ABCS	−5.2
Boiling Point at 1 atm (°C)	
A	287
S	100.0
D	77.8

the user to uncover alternatives that can be considered a combination of the two techniques. The alternative depicted in Figure 5g is an example where both cooling and evaporative crystallizers are present. Therefore, we do not restrict ourselves to existing conventional schemes. Another advantage of the procedure is that it is not limited to processes where we want complete recovery of all solutes as pure components. This point will be demonstrated in Example 3.

Flowsheet alternatives using MSA

The generation of flowsheet alternatives using MSA follows the same steps in Table 3, except that Step 1 also includes the selection of an MSA. Additional rules as listed in Table 7 are to be used along with the ones in Table 6. The procedure is now discussed alongside Example 2, where we consider the complete recovery of an organic compound *A* and two amino acids *B* and *C* from an aqueous solution (Takano et al., 1999). According to the reported experimental data, the phase diagram for this system mimics the one depicted in Figure 3. The assumed input information is listed in Table 8.

Step 1: Definition of Separation Objectives and Construction of Phase Diagrams. Table 9 shows the classification of MSAs according to their role in effecting separation. In addition to its impact on solubility, ease of recovery is an important consideration in choosing an MSA.

Class I MSAs selectively change the solubility of one or more components. Examples include acids, bases, and hydrotropes. To minimize the energy requirement in a distillation recovery process, it is desirable that the solvent has a low heat of vaporization (less than 800 kJ/kg) and a low specific heat (less than 3 kJ/kg·K) (Ireland, 1985). The liquid MSA should have a high relative volatility with respect to the solvent and does not form any azeotrope with it. Class II MSAs affect solubility, as well as cause liquid-liquid phase split at some compositions and temperatures. This phase split feature can be utilized to facilitate the MSA recovery.

A class III MSA crystallizes the desired component by forming a precipitating adduct. The adduct must be easily decomposable to recover the MSA and yield the desired product. Distillation is commonly used to separate the product from the adductive agent (Dale, 1981). Class III MSAs also include reactive agents, which form a desirable product with one of the components. An example of class IV MSA is a solvent, which is added simply to provide an additional degree of freedom. It is especially useful for the complete separation of a two-solute system in extractive crystallization (Rajagopal et al., 1991). Without an extra solvent, movements in composition space are restricted to a straight line and there is no way to cross the binary eutectic. In the following discussion, the term ''MSA''refers to the first three classes of MSA, and class IV is simply referred to as ''solvent''.

Step 1 for Example 2: The objective is to completely separate all three solutes. Figure 6a reveals that the projected area of the eutectic surface *AC-ABC-ABCS-ACS* is very narrow. Thus, crossing this boundary using solvent removal or addition is difficult. For this reason, we consider using MSA to assist separation. Experiments show that the solubility of *A* increases significantly as the pH becomes neutral, while the solubilities of *B* and *C* are not much affected (Takano et al., 1999). This leads to the use of a base *D* as an MSA to bring about the pH change (Rule 16). The isoplethal cut at 5% *D* corresponds to $\mathrm{pH} = 7$.

Step 2: Construction of Separation Core Structure. In this step, we determine the number of crystallizers and the need for purging. When liquid-liquid immiscibility is involved, the composition of mother liquor might fall on an invariant point such as one of the apexes of a solid-liquid-liquid equilibrium triangle (an example will be seen in Figure 8), meaning that its composition would not change even if a recycle stream is present. Consequently, recycle is not useful to avoid product loss. Unless recycling is desired for other reasons, such as to adjust the viscosity of the slurry, the mother liquor must be totally purged.

Step 2 for Example 2: We need three crystallizers to recover *A*, *B*, and *C* as pure components (Rule 1). Since everything is recovered, purging is not necessary (Rule 3).

Step 3: Selection of Separation Sequence and Unit Operations. The selection of separation sequence should take the MSA into consideration, because addition or removal of MSA serves as an additional alternative for crossing the process boundaries. In this step, we also consider unit operations to recover the MSA (Table 9) and assign the destinations of the separated streams. The MSA is often used only in a particu-

Table 9. Classification of MSA for Crystallization-Based Separation Processes

Class	Purpose of MSA Addition	Preferred Method of MSA Recovery
I	Change the relative solubilities of the components	Distillation
II	Change the relative solubilities of the components and induce liquid-liquid phase split	Decantation or extraction
III	Form a crystallizing adduct or a desirable product with one of the components	Distillation or not recovered
IV	Provide additional degrees of freedom	Distillation

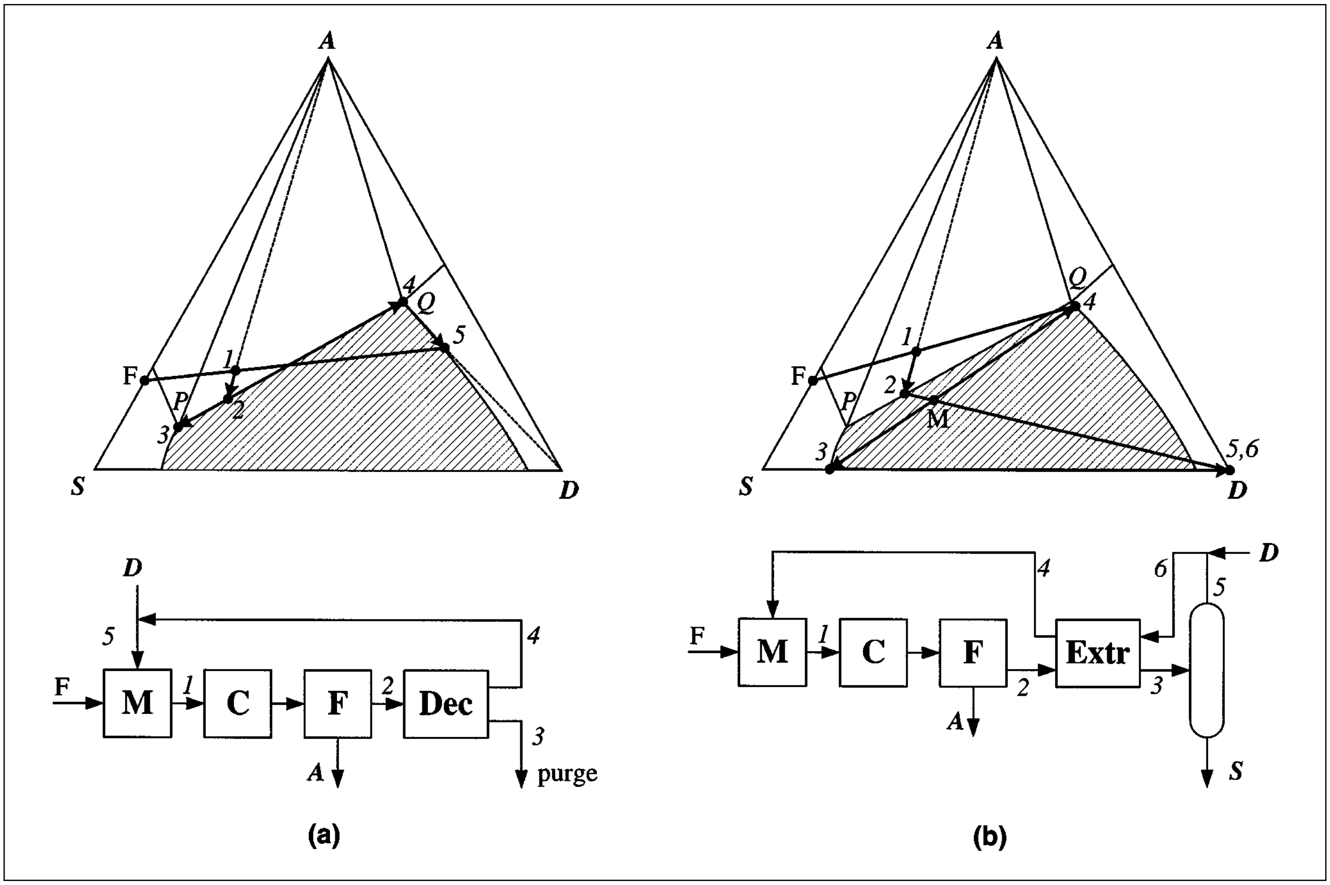


Figure 8. Flowsheet alternatives for recovering a heat-sensitive compound (Example 4).

(a) Using a decanter; (b) using a multistage extractor.

lar section of the process, which can include one or more crystallizers.

For a class II MSA, Berry et al. (1997) discussed a number of process options. One can use a multistage extractor instead of a decanter. Depending on the phase behavior, a multistage extractor may improve the recovery of the MSA. Another alternative is to perform extraction before crystallization to improve the yield.

Step 3 for Example 2: In the following discussion, we will refer to the compartments at 0% and 5% *D* cuts using subscripts “0” and “5”, respectively. Since the feed is in compartment A_0 (Figure 6a), it is advisable to separate *A* first (Rule 4). However, we can also consider the alternative of using MSA at the beginning of the separation train. Upon addition of 5% *D*, the feed is brought to compartment C_5. For this reason, we can alternatively choose to separate *C* first. Therefore, we have four possibilities of separation order, namely *A-B-C, A-C-B, C-B-A*, and *C-A-B*. In this example, we focus on the *C-A-B* option, which turns out to be the best choice. We will also describe briefly two other options, and show why they are not favorable.

Figure 6a shows the process paths for the *C-A-B* option and the corresponding step 3 flowsheet. The development of this figure is depicted in Figures 6b–6d. First, the MSA is added to the beginning of the separation train (Rule 22). We now focus on the projections of the eutectic surfaces at 5% *D* (Figure 6b). *C* is crystallized in the first crystallizer, whose output (point *3*) must lie within compartment C_5. We then move point *3* to point *4* in compartment A_0 using MSA removal (Rule 23). Since the MSA (*D*) has a lower boiling point than water, we can use a flash column for MSA removal. The recovered MSA should be recycled (Rule 24). At this point, we switch our attention to the projections at 0% *D* (Figure 6c). The composition after crystallizing *A* (point *5*) must lie on the projection of eutectic surface *AB-ABC-ABCS-ABS*. Solvent removal is then used to move from compartment A_0 to B_0 (Rule 7). The final mother liquor (point *7*) must lie within compartment B_0 (Figure 6d). This stream is mixed with the feed to give point *1*.

The option of using *A-B-C* separation order is illustrated in Figure 6e. Because the process points are very close to one another, part of the phase diagram has been exaggerated to maintain the clarity of the presentation. After recovering component *A*, we use solvent removal to move point *2* in compartment A_0 to point *3* in compartment B_0 (Rule 7), and add MSA to move point *4* in compartment B_0 to compartment C_5 (Rule 23). The process paths must satisfy several restrictions. The output of the first crystallizer (point *2*) must lie on the projection of eutectic surface *AB-ABC-ABCS-ABS*. Point *4* must lie on the extension of line *B-2* within compartment B_0. It must also move to compartment C_5 upon addition of 5% *D*. The composition after crystallizing C (point *6*) must lie on the extension of line *C-4* and yield point *1* on line *A-2* when combined with F. All these restrictions can only be satisfied if these points are located close together, as shown in Figure 6e, meaning that their compositions do not differ by much. Consequently, the required flow rates for treating a given amount of feed would be prohibitively high.

Figure 6f depicts the process paths following the *A-C-B* separation order. After recovering A, MSA addition is used to cross from compartment A_0 to C_5, that is, point *2* to point *3* (Rule 23). The boundary between compartments C_5 and B_5 is crossed using solvent removal, that is, point *4* to point *5*. The problem with the flowsheet in Figure 6f is that water must be removed in the presence of D (between points *4* and *5*). This is not desirable since D has a lower boiling point than water, so that distillation cannot be used.

Step 4: Addition of Unit Operations for Proper Plant Operations. In this step, we specify additional units, if necessary, to ensure proper plant operations. Necessary unit operations are added to reduce purge losses, remove insoluble impurities, and decompose any intermediate product formed in the process to give the desired final product.

Step 4 for Example 2: There is no need for additional solvent addition or removal units for the *C-A-B* option (Rules 10, 11, 27). A distillation column is used to recover the MSA from stream 3 (Rule 26).

Step 5: Selection of Crystallizer Type. The presence of an MSA creates a restriction on the use of evaporative crystallizers. If the MSA is more volatile or just slightly less volatile than the solvent, it will evaporate along with the solvent. This is often undesirable, unless the MSA has to be removed at the same time. Irrespective of crystallizer type, the MSA can be directly added to the crystallizer, or the feed and MSA are pre-mixed in a mixer preceding the crystallizer.

Step 5 for Example 2: Rule 13 leads to operation at the highest practical temperature for the third crystallizer (C3). The other two crystallizers should be operated at the lowest practical temperature (Rule 12). Since the melting points of the solutes are higher than the normal boiling point of water, we want to consider using evaporative crystallizers (Rules 14, 15). Considering the feasible temperature range at which water can be evaporated, we choose the lowest and highest practical temperatures to be 80°C and 110°C, respectively. An evaporative type is not suitable for the first crystallizer since an MSA that is more volatile than the solvent is present (Rule 30). Since there is no need for evaporation, C1 can actually be operated at an even lower temperature. However, since experimental data show that the solubility of C at 80°C is sufficiently low and is not significantly affected by a further decrease in temperature, we choose to operate this crystallizer at 80°C. The final flowsheet (Figure 6d) is similar to the one proposed by Takano et al. (1999). We also have the alternative of sending streams 7 and 8 directly to C1 without using a mixer (Rule 31), if kinetics and mass-transfer limitations are absent.

Additional Examples

To show how the procedure can be applied to different types of industrial systems, five additional examples are considered. Again, we focus on Steps 1 to 5.

Example 3: Recovery of adipic acid

This example illustrates how the flowsheet would have been different if the separation objective were changed. Consider the three-solute-system discussed in Example 1, but now we only want to recover A, while B and C are to be purged. An industrial process represented by this example is the recovery of adipic acid (A) from two other impurities, namely succinic acid (B) and glutaric acid (C). Figure 5a mimics the thermodynamic behavior of an aqueous solution of these dibasic acids (Cesar and Ng, 1999). Figure 7a shows two isothermal cuts at T_{C1} and T_{C2}, which are the upper and lower limits, respectively, of the practical operating temperature range. The final flowsheet is depicted in Figure 7b.

Step 1: Since there is no incentive for separating B and C, the separation objective is to recover only A.

Step 2: We definitely need a crystallizer to recover pure A (Rule 1). We notice from the phase diagram that the concentration of A in the mother liquor (point *2*) is about 20%, and purging can lead to a significant loss of this component. To avoid the potential loss, we can recycle all of the mother liquor while removing B and C from the process as solids. We need another crystallizer for recovering B and C together (Rule 2).

Step 3: Since the feed is in compartment A, we separate A first (Rule 4). B and C are then crystallized together in the second crystallizer along the BC double-saturation curve (*BC-ABC*). Because of the location of point *2*, it is convenient to cross from compartment A to C. Since $T_{C1} > T_{C2}$, the solubility surfaces at T_{C1} are below those at T_{C2} with respect to the solvent apex (see the tetrahedron phase diagram in Figure 2b). Therefore, solvent addition should be used to move point *2* in compartment A to point *3* in compartment C (Rule 7).

Step 4: Since the feed already contains solvent and there is no solvent removal or purge stream in the separation train, it

Table 10. Input Information for Recovering a Heat Sensitive Compound (Example 4)

Feed Composition (mole fraction)	
A	0.20
S	0.80
Pure Component Melting Point (°C)	
A	(Decomposes before Melting)
D	−72.9
S	0.0
Binary Eutectic Temperature (°C)	
AS	−7.0
Binary Eutectic Composition (mole fraction)	
A	0.15
S	0.85
Range of Allowable Temperature (°C)	
A	30 (max.)
D	No Limit
S	No Limit
Boiling Point at 1 atm (°C)	
D	85.7
S	100.0
Solubility of A in S (Without Presence of D)	
at 30°C	0.3 kg *A*/kg *S*
at 5°C	0.27 kg *A*/kg *S*

is necessary to add a solvent removal unit after the second crystallizer (Rule 11).

Step 5: In agreement with Rule 13, the first crystallizer (C1) has to be operated at the higher temperature (T_{C1}), while the other one (C2) at the lower temperature (T_{C2}). As in Example 1, since the boiling point of the solvent is much lower than the melting point of B (Rule 14) and the solvent has a high relative volatility (Rule 15), an evaporative type can be used for C1.

Example 4: Recovery of a heat-sensitive solute

In this example, the generation of flowsheet alternatives using liquid-liquid phase split is illustrated. Such a process is useful to recover biochemical and pharmaceutical products, which are often heat sensitive. Let us consider the recovery of a heat-sensitive component (A) from a solution that only contains A and a solvent S. The input information is given in Table 10.

Step 1: Since the solubility of A in S at the allowable temperature range is relatively high (about 0.3 kg A/kg S), evaporation of solvent would be necessary to obtain high yield. However, considering the high normal boiling point of the solvent (100°C), evaporation in a feasible pressure range will subject the product to a temperature above the allowable limit (30°C). Therefore, we choose to use a separation process using an MSA. Either a class I or class II MSA can be used (Rules 16 and 18). Here, we consider an MSA that induces liquid-liquid immiscibility (D). An isothermal cut at the operating temperature, chosen to be 25°C, is shown along with the process paths for two alternatives (Figures 8a and 8b).

Step 2: The core structure consists of only one crystallizer, since there is only one product to be recovered (Rule 1). We aim for complete recovery for the solute, but as will be discussed in Step 4, it is not possible. Therefore, partial purging is necessary (Rule 3).

Step 3: There is no separation sequence and no separation boundary to cross. MSA is introduced before the first crystallizer to move the feed into the saturation region of A (Rule 22). For this system, we can use a decanter or a multistage extractor for MSA removal (Table 9).

Step 4: Figure 8a shows the flowsheet alternative with a mixer and a decanter. The decanter splits the crystallizer outlet (point *2*) into two streams. It is desirable to recover A from the solvent-rich stream (stream 3). This can be achieved by sending this stream to a solvent removal unit (Rule 11), removing some solvent from the process, and recycling the remainder to the crystallizer. However, this option is not feasible because A might decompose in the distillation unit. Furthermore, since the composition of stream 3 falls on an invariant point (P), partial recycle will not be useful and this stream has to be purged (Rule 21). Stream 4 is the MSA-rich stream, which should be recycled (Rule 24). Because an amount of D is purged in stream 3, a makeup stream of fresh D should be added to this recycle stream.

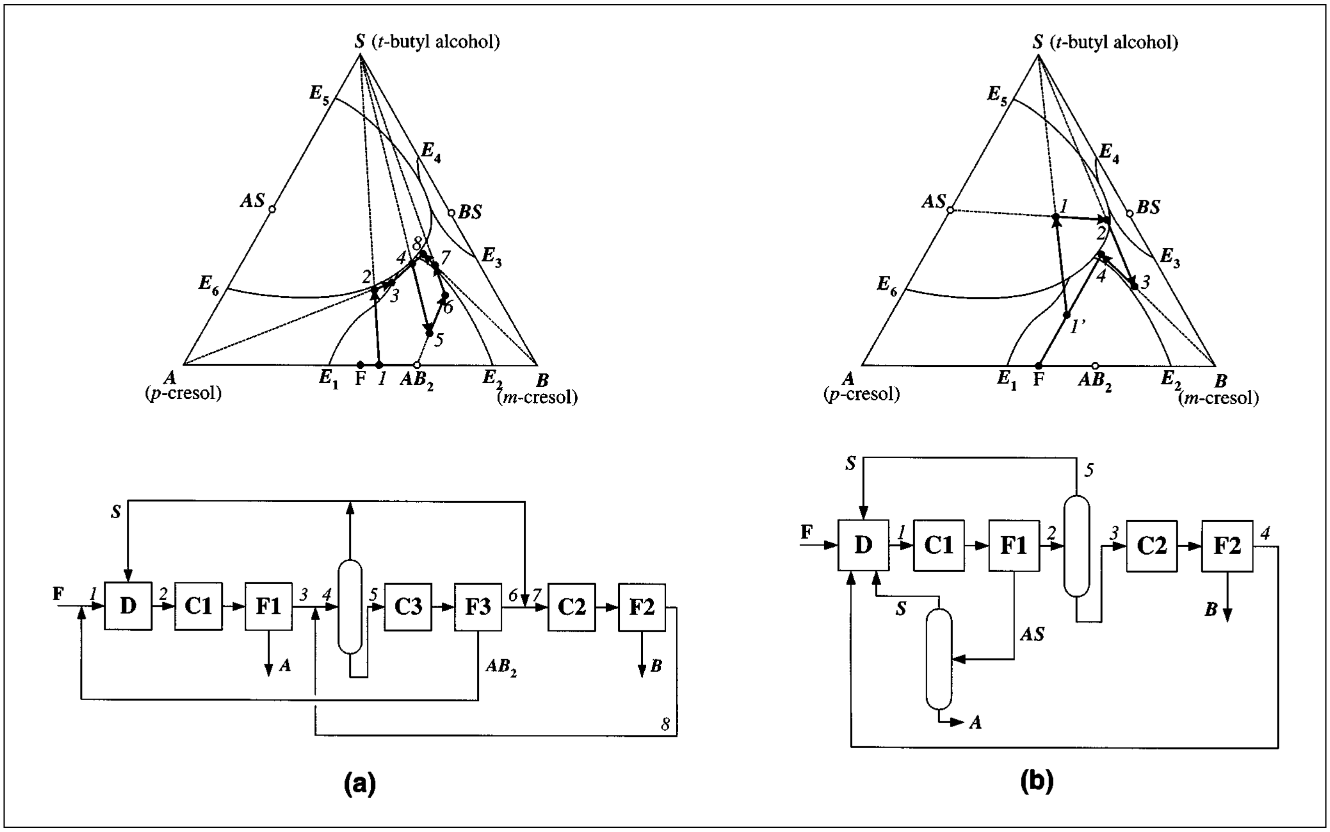


Figure 9. Flowsheet alternatives for separating *p*-cresol and *m*-cresol (Example 5).

(a) By crystallizing an intermediate compound; (b) by crystallizing an adduct.

Figure 8b depicts the alternative of using a multistage extractor. Stream 2 is contacted countercurrently with D, and two streams (3 and 4) are produced. The number of stages in the extractor can be adjusted so that the solvent-rich stream contains little A. We assume that a complete recovery of A can be achieved, and recycle of this stream is unnecessary. Before purging, stream 3 is sent to a solvent removal unit (Rule 26) to recover MSA. The MSA-rich stream from the extractor (stream 4) is recycled.

Step 5: For both alternatives, evaporative crystallizer is not an option because the MSA is more volatile than the solvent (Rule 30). We can add the MSA directly to the crystallizer (Rule 31), which eliminates the need of a mixer.

Example 5: Separation of p- and m-cresols

This example illustrates the generation of flowsheet alternatives for systems in which intermediate compounds are formed. It is desired to separate *p*- and *m*-cresol from a 50:50 mixture. Crystallization is an attractive technique because *p*-cresol (A) and *m*-cresol (B) are close boilers (both having a boiling point of 202°C), while their melting points differ quite significantly (35°C for *p*-cresol and 10.9°C for *m*-cresol). The binary system of these isomers forms a compound (AB_2) with a congruent melting point at 33.3% A. The two eutectics are located at 12.5% and 60% A. The presence of the eutectics prohibits complete separation without an MSA. Therefore, we add a solvent (class IV MSA) to obtain an additional degree of freedom to work with (Rule 20). Tare and Chivate (1976) proposed *t*-butyl alcohol (S), which forms an adduct with both isomers. The polythermal phase diagram for the ternary system is shown in Figure 9.

We need two crystallizers to separate A and B (Rule 1). Since there is no impurity present in the feed, purging is not necessary (Rule 3). The feed is located in compartment AB_2, which is not one of the desired products. According to the separation objective, we must visit compartments A and B. The phase diagram reveals that the feed can be brought to compartment A by adding S (Figure 9a). For this reason, we separate A first and then B, and we have to move from compartment A to B. However, it is not possible to do so by solvent addition or removal, because the two compartments are not adjacent to each other. There are two options to deal with this problem. The first is crystallizing AB_2, whose compartment is adjacent to both compartments A and B (Rule 6). The second is crystallizing AS, which is an adduct that can be easily separated using distillation. Note that compartment AS is also adjacent to both compartments A and B. Let us consider the two alternatives one by one.

The flowsheet alternative of crystallizing AB_2 is depicted in Figure 9a. To crystallize this intermediate component, another crystallizer (C3) is added between the first and second crystallizers. We try to use solvent removal to cross the boundary between compartments A and AB_2, and solvent addition to move from compartment AB_2 to B (Rule 7). If solvent removal only were used to cross from compartment A to AB_2, point *5* would have been located on the left side of point AB_2. Consequently, it would not have been possible to obtain point *6* which is located near the boundary between compartments AB_2 and B. For this reason, we use a stream combination (combining streams 3 and 8) to yield stream 4 (Rule 9). A dissolver is needed at the beginning to introduce solvent S to the feed (Rule 22). We do not use evaporative crystallizers in this process because the boiling point of *t*-butyl alcohol (82.9°C) is substantially higher than the melting points of A and B (Rule 15).

Figure 9b shows the flowsheet alternative using adduct formation. Only two crystallizers are needed in this alternative. Instead of crystallizing A in the first crystallizer, we recover the adduct AS. We use solvent removal to cross from compartment AS to B (Rule 7) and add a dissolver to introduce solvent S to the feed (Rule 22). A distillation column is added to recover A from the adduct (Rule 29). S is recycled back to the dissolver. For the same reason as described above, evaporative crystallizers are not used.

Example 6: Separation of chlorobenzoic acids using a hydrotrope

This example illustrates the use of the procedure for a separation process using a hydrotrope. Colônia et al. (1998) investigated the separation of a solid mixture of *o*- and *p*-chlorobenzoic acids (CBA). These acids are sparingly soluble in water, but their solubilities are greatly augmented by the addition of a suitable hydrotrope, sodium butyl monoglycol sulfate (NaBMGS). Figure 10a shows two cuts of the phase diagram, taken at different temperatures and hydrotrope concentrations. We want to construct a flowsheet for separating a mixture of 30% *o*-CBA (A) and 70% *p*-CBA (B) into its pure components.

The final flowsheet is given in Figure 10b. We need a solvent (type IV MSA), which provides an additional degree of freedom (Rule 20), and also an MSA that selectively affects the solubility of the desired products (Rule 16). In this case, water (W) is used as the solvent and the hydrotrope (H) as the MSA. Two crystallizers are needed (Rule 1), and purging is not necessary since there are no impurities in the feed (Rule 3). The solid mixture is completely dissolved by adding water and NaBMGS, producing stream F. Since this point is in the saturation region of B at $C_{H,1}$ and T_1 (Figure 10a), we choose to crystallize B first (Rule 4). This is achieved by adding water to change the hydrotrope concentration to $C_{H,1}$. Next, we notice that point *2* would move to the saturation region of A at a lower hydrotrope concentration ($C_{H,2}$), which we assume to be zero. Therefore, a suitable MSA removal unit must be identified and added (Rule 23). To avoid co-precipitation, the hydrotrope removal must be done at a higher temperature (T_2). Figure 10a also reveals that water must be removed in order to move from point *3* to point *4* and crystallize A. We add a dissolver at the beginning of the train to introduce the MSAs (Rule 22) Additional water is directly added to the first crystallizer (C1) (Rule 31). an evaporative type is used for the second crystallizer (C2), since the melting points of the CBAs (141°C and 242°C) are much higher than the boiling point of water (Rule 14) and there is no MSA present in this part of the process (Rule 30).

Example 7: Calcium carbonate and magnesium oxide from dolomitic materials

Let us now consider an example in which reactive crystallization is involved. It is desired to obtain calcium and magnesium compounds from dolomitic materials such as dolomite calcine (a mixture of CaO and MgO) (MacIntire, 1938). Both oxides can form hydroxides in their aqueous solutions, but MgO has a much lower solubility than CaO. Therefore, it is convenient to use water as a solvent (class IV MSA) for this separation process. MgO is considered as an insoluble impurity, although in reality it is present in a very small amount in the solution. Since calcium carbonate ($CaCO_3$) is an important industrial product with many applications, we want to obtain this compound by reacting CaO with CO_2, which serves as a reactive MSA (class III) (Rule 19). $CaCO_3$ is only slightly soluble in water, but its solubility is further decreased by the presence of NH_3. For this reason, we also want to use gaseous NH_3 as a class I MSA (Rule 16). A possible phase diagram is sketched in Figure 11a. For this reactive system, we use a set of reaction-invariant transformed coordinates (Ung and Doherty, 1995; Berry and Ng, 1997; Samant and Ng, 1998). We consider four components in the transformed coordinates: CaO (A), CO_2 (B), $CaCO_3$ (C), and water (S), and one reaction: $A + B \rightarrow C$. MgO is not included in the phase diagram, since it is considered completely insoluble. Two saturation curves are shown; the first is when NH_3 is not present, and the other is with 10% NH_3.

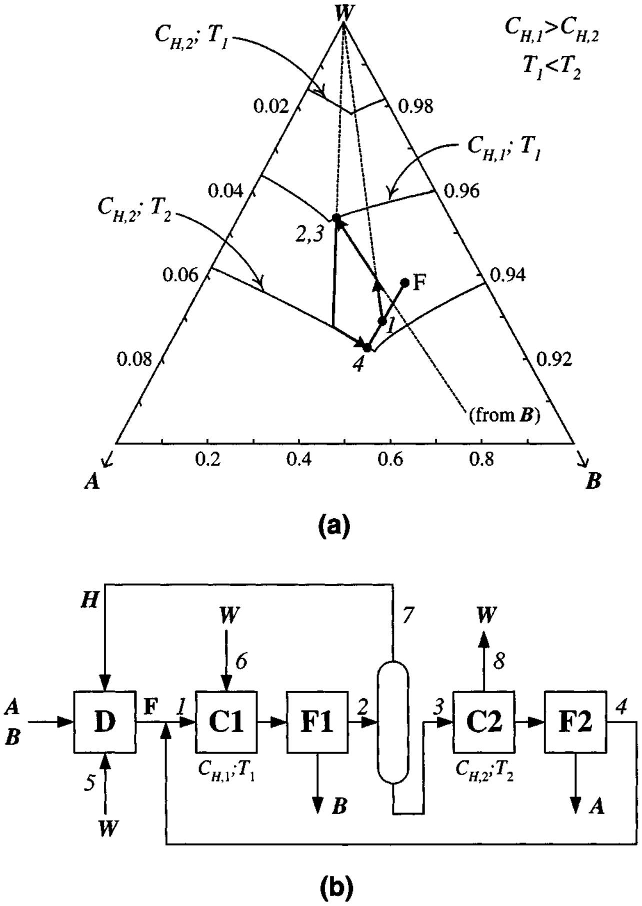


Figure 10. A flowsheet alternative for separating chlorobenzoic acids (Example 6).

(a) Isothermal, isoplethal cuts of the phase diagram; (b) flowsheet structure.

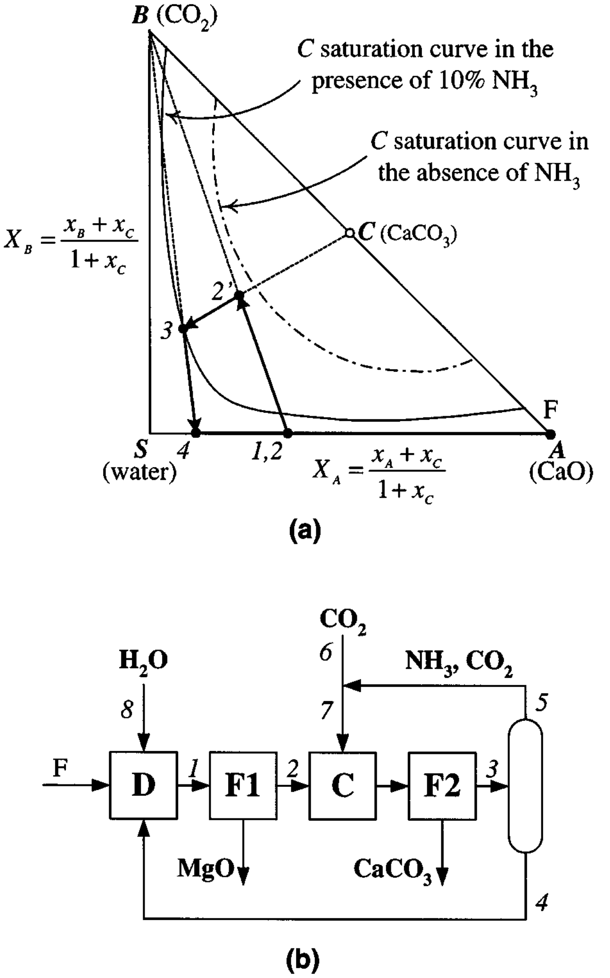


Figure 11. A flowsheet alternative for production of calcium carbonate and magnesium oxide (Example 7).

(a) Phase diagram; (b) flowsheet structure.

Figure 11b depicts the flowsheet for this process. We use one crystallizer for recovering calcium carbonate (Rule 1). Purging is not necessary since the only impurity present is MgO, which is recovered as a solid (Rule 3). Water is added to a dissolver at the beginning of the process (Rule 22). A gas stream containing CO_2 and NH_3 (stream 7) is fed to the reactive crystallizer to move point 2 into the saturation region of C (point $2'$), causing C to crystallize. The composition then moves to point 3. We need a separation unit to remove NH_3 from the mother liquor (Rule 26). Due to the low solubility of NH_3 in water at elevated temperatures, a flash tank would be adequate for this purpose. Unconverted CO_2 is also separated to the gas stream (stream 5), causing the solution composition to move to point 4. Stream 5 is recycled to the crystallizer (Rule 24). To separate MgO, we must add a filter right after the dissolver (Rule 28). Since gaseous MSAs are added to the reactive crystallizer, we do not use an evaporative crystallizer (Rule 30).

Step 6: Evaluation of Flowsheet Alternatives

In Step 6 of the unified procedure, we select the best feasible process among the alternatives we have generated. There are two sub-steps. In the first, we determine the number of design variables by a degree of freedom analysis and select an appropriate set of design variables. The range of the design variable values which does not violate practical or material balance constraints should be determined. For example, if we select the amount of solvent evaporated in a crystallizer as a design variable, we have to consider the restriction imposed by the increasing slurry viscosity as more solvent is removed. If the composition of a stream is chosen as a design variable, we always have to make sure that the selected composition does not cause any flow rate to become negative, and that each process point is located in an appropriate compartment.

There exist geometric constraints, related to the phase behavior, which can be used to guide process synthesis. This is illustrated with the process alternative using a multistage extractor (Figure 8b). In this configuration, the design variables are the compositions of streams 2 and 4. By solving the material balance around the extractor, the following expression for $x_{A,3}/x_{S,3}$ is obtained

$$\frac{x_{A,3}}{x_{S,3}} = \frac{x_{A,2}(1-x_{S,4}) - x_{A,4}(1-x_{S,2})}{x_{S,2}(1-x_{A,4}) - x_{S,4}(1-x_{A,2})}. \tag{5}$$

Clearly $x_{A,3}$ and $x_{S,3}$ cannot be negative and the righthand side of Eq. 5 must be greater than or equal to zero. We further notice that any straight line passing through point A can be represented by $x_S/(1-x_A) = \text{constant}$, which has a value between zero and one. Specifically, line AD is represented by $x_S/(1-x_A) = 0$ and line AS by $x_S/(1-x_A) = 1$. Since stream 4 always contains more D than stream 2, it must be true that line A-4 is always closer to AD than line A-2, that is

$$\frac{x_{S,2}}{1-x_{A,2}} > \frac{x_{S,4}}{1-x_{A,4}}. \tag{6}$$

This implies that the denominator of the righthand side of Eq. 5 is always positive. Consequently, the numerator should be non-negative, or

$$\frac{x_{A,2}}{1-x_{S,2}} \geq \frac{x_{A,4}}{1-x_{S,4}} \tag{7}$$

Geometrically, the inequality of Eq. 7 implies that point *2* should always be above the line connecting *S* and *4*, and the equality implies that points *S*, *2*, and *4* are collinear. If it is desired that stream 3 contains no A ($x_{A,3} = 0$), the two sides of Eq. 7 are equal (because of Eq. 5). Since point *2* should always lie on line *PQ* and point *4* should always fall on the LLE curve below *Q*, this means that line *PQ* must be able to intersect line *S-4* for the equality to hold. This geometric constraint can be used to quickly screen whether it is possible to set $x_{A,3} = 0$.

In the second sub-step of Step 6, the economics of each feasible flowsheet alternatives is evaluated. This is illustrated with the production of salt (Example 8). Sodium chloride, NaCl, is mainly produced from either seawater or deposits on land (Rousseau, 1994). Let us consider a process for recovering NaCl using the latter method. Water is pumped into the mine to dissolve the solid salt, as well as a small amount of impurities, and the solution is then crystallized to produce salt crystals. Table 11 shows the input information for this example.

Table 11. Input Information for the Production of Salt (Example 8)

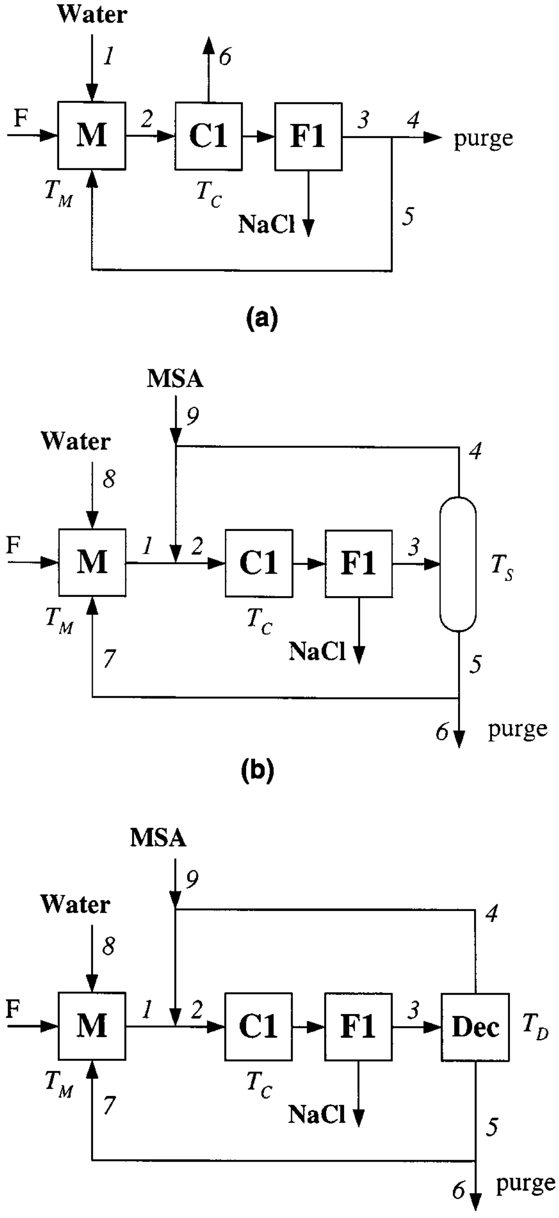
Physical Properties of NaCl	
Melting point	800.4°C
Enthalpy of crystallization	$500\ \text{kJ}\cdot\text{kg}^{-1}$
Crystal density	$2{,}000\ \text{kg}\cdot\text{m}^{-3}$
Physical Properties of Water	
Heat of vaporization	$2{,}360\ \text{kJ}\cdot\text{kg}^{-1}$
Specific heat	$4.2\ \text{kJ}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$
Properties of NaCl-H_2O System	
Incongruent melting point of NaCl.2H_2O	0.15°C
Solubility of NaCl in water (Perry et al., 1997)	$S = 0.357 + 0.00041T$ kg/kg H_2O (T in °C)
Specific heat of aqueous NaCl solution (Perry et al., 1997)	$C_p = 4.135 - 3.1158\,x_A\ \text{kJ}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$ (x_A = weight fraction)
Solution density	$1{,}000\ \text{kg}\cdot\text{m}^{-3}$
Physical Properties of Acetone	
Heat of vaporization	$500\ \text{kJ}\cdot\text{kg}^{-1}$
Specific heat	$1.04\ \text{kJ}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$
Boiling point at 1 atm	56.10°C
Relative volatility (water = 1)	4
Properties of NaCl-H_2O-2-Propanol System (Figure 13a)	
Composition of invariant points at 25°C (Gomis et al., 1994)	
Aqueous phase (point L_1)	7.5% PrOH; 21.3% NaCl; 71.2% water
Organic phase (point L_2)	75.5% PrOH; 1.7% NaCl; 22.8% water
Properties of NaCl-H_2O-DiPA System (Figure 13b)	
Composition of invariant points at 25°C (Weingaertner et al., 1991)	
Aqueous phase (point L_1)	0.6% PrOH; 26.0% NaCl; 73.4% water
Organic phase (point L_2)	93.2% PrOH; 0.1% NaCl; 6.7% water

We begin by developing the process alternatives. A solvent (in this case, water) is needed to obtain an additional degree of freedom (Rule 20). The phase behavior of the NaCl-H_2O system shows the presence of a hydrate (NaCl.2H_2O) which has an incongruent melting point at 0.15°C (Mullin, 1993). Below this temperature, the hydrate is crystallized out. Pure NaCl can only be precipitated from the solution above this temperature. In the range of 0–200°C, the solubility of NaCl varies only slightly with temperature (Perry et al., 1997). Therefore, Rules 16 and 17 suggest the use of another MSA in addition to water. Alternatives with and without using an additional MSA will be explored.

We first consider the alternatives without using an MSA. The flowsheet is shown in Figure 12a. Only one crystallizer is needed (Rule 1), and partial purging is required since impurities are present (Rule 3). Since the solubility of NaCl increases as temperature increases, we should operate the crystallizer at a lowest practical temperature (Rule 12). Due to the high melting point of NaCl and the fact that water is much more volatile than NaCl, we have the option of using an evaporative crystallizer (Rule 15). Note that if the flow rate of stream 6 is zero, we have a cooling crystallizer.

Next, we consider MSAs that can reduce the solubility of NaCl in water (Rule 16). Three organic solvents are potential candidates. Acetone, which has a low heat of vaporization, a low specific heat, a high relative volatility with respect to water, and does not form azeotropes with water, falls into class I. Other candidates are 2-propanol (PrOH) and diisopropylamine (DiPA), which belong to class II (Hanson and Lynn, 1989; Weingaertner et al., 1991). Figures 12b and 12c show the flowsheets for the processes using a class I MSA (acetone) and a class II MSA (PrOH or DiPA), respectively. The phase behaviors of these systems at 25°C are depicted in Figure 13. The flowsheet structure includes one crystallizer, and a purge stream is needed. We add an MSA addition unit prior to the crystallizer (Rule 22). An MSA recovery unit should be placed after the crystallizer (Rule 26). The choice of the MSA recovery unit depends on the MSA (Table 9). The water-rich stream (stream 7) is recycled to the mine. Due to loss in the purge, fresh water (stream 8) and MSA (stream 9) must be added. The immiscibility between water and DiPA (without the presence of NaCl) at 25°C suggests the use of a multistage extractor to obtain an MSA-free aqueous phase (as in Example 4). However, it is not possible to obey the constraint described in Eq. 7, so the option is not feasible.

Table 12 summarizes the alternatives and lists the design variables and the key material balance equations for each alternative. The crystallizer temperature T_C(°C) determines the composition of crystallizer output (stream 3). The choice of T_C depends on various factors. For example, Weingaertner et al. (1991) stated that it is better to operate the crystallizer at a temperature where only one liquid phase is present, probably due to the belief of having better mixing. The evaporation ratio f_e (in the alternatives without MSA) is defined as the fraction of water entering the crystallizer being evaporated, that is, $F_6/(F_2 x_{S,2})$. The recycle ratio f_r is defined as the fraction of the water-rich stream being recycled (F_5/F_3 in the alternatives without MSA and F_7/F_5 in the alternatives using MSA). The effective dissolution temperature in the mine T_M (°C) is assumed to be fixed. Using these equations, it is possible to evaluate the economics of the flowsheet alternatives.



(a)

(b)

(c)

Figure 12. Flowsheet alternatives for the production of salt (Example 8).

(a) Without MSA; (b) with a class I MSA; (c) with a class II MSA.

The values of the key design variables and parameters used in the economic evaluation are listed in Table 13. In the alternative using a cooling crystallizer, the crystallizer temperature has been chosen to be as low as possible but slightly above the minimum temperature at which crystals of pure NaCl can be obtained (0.15°C). In the alternative using an evaporative crystallizer, we choose f_e to be 0.25 by considering the maximum slurry viscosity that can be handled. The crystallizer is operated at 50°C, considering the high cost of vacuum to operate below this temperature. A purity level of 99.5% is assumed for the distillation column in the alternative using acetone. For the alternatives utilizing liquid-liquid phase split (using 2-propanol and DiPA), the crystallizer is operated at a much lower temperature compared to the decanter in order to enhance product yield (Rule 12).

We can now compare the Total Annualized Costs (TACs) of these alternatives using a capital charge factor of 1/3 years. Shortcut equipment models suggested by Douglas (1988) are used along with equipment and energy cost data from Peters and Timmerhaus (1980). Only the major components of equipment and energy costs are taken into account in this preliminary evaluation. Figure 14 shows the relative TACs of the five alternatives, using the conventional industrial process with evaporative crystallizer as the base case. The TAC for alternatives using MSA is presented as a function of the amount of MSA used.

As expected, the TAC for the alternative using cooling crystallizer is much higher compared to the base case. With an approximately 2% recovery of the NaCl in the feed, the recycle stream is large and a large crystallizer is needed. The alternative of using acetone offers a lower cost when $x_{D,3} > 0.15$. This is primarily due to a lower energy requirement for acetone/water distillation as compared to water evaporation and steam ejectors in the base case. For low concentrations of acetone, the solubility of NaCl in water is not substantially affected. Therefore, the TAC approaches the TAC for cooling crystallizer as $x_{D,3}$ decreases to below 0.15. For processes using immiscible drowning-out agents (2-propanol and DiPA), we observe an optimal value of $x_{D,3}$ which leads to a minimum in TAC. It is apparent that the use of MSA can lead to a significant decrease in TAC.

We now compare in more detail the economics of the two different MSA alternatives, which is dictated by the phase behavior. As indicated by Eq. 14, the crystallizer size is determined by the compositions of aqueous and organic streams leaving the decanter (streams 4 and 5), and the cost related to the crystallizer is the single dominating factor for both alternatives. Let us first consider the NaCl/H_2O/2-propanol system (Figure 13a). As $x_{D,3}$ increases, the composition of stream 5 moves towards L_2 along the aqueous-phase LLE curve (L_1P), while that of stream 4 moves towards L_1 along the organic-phase LLE curve (L_2P). As a consequence, the concentration of NaCl in stream 5 slightly decreases, and the water content in stream 4 rapidly increases. As pointed out by Weingaertner et al. (1991), high water content in the organic phase leads to a high flow rate of this recycle stream. The behavior of TAC vs. $x_{D,3}$ is different for the NaCl/H_2O/DiPA system (Figure 13b). Since the decrease in solubility due to the addition of DiPA is not as significant as in the case of 2-propanol, a large MSA recycle stream is required and the TAC of this alternative becomes very high for low values of $x_{D,3}$. However, as $x_{D,3}$ increases, the salt content of stream 5 decreases significantly. This means more salt can be dissolved and a smaller crystallizer is required. Obviously, there is a limit on how much MSA can be used. If the MSA content is too high ($x_{D,3} > 0.7$), the TAC again increases due to the large recycle flow of the MSA.

The results clearly show that the use of MSA (especially DiPA) can lead to a significant reduction in cost, compared to the conventional evaporative crystallization technique. The reduction is mostly due to the elimination of the energy-intensive water evaporation step. Clearly, a more detailed evaluation accounting for equipment units for heat exchange and purification of MSA before recycling (extractor and steam stripper) can be performed (Weingaertner et al., 1991). Although we may obtain different optimum operating conditions from such an evaluation, it is unlikely that it would affect the conclusion on which is the best alternative.

Conclusions

A unified procedure summarized in Figure 15 for the design of crystallization-based separation processes has been

Table 12. Design Equations for Alternatives Considered in the Production of Salt

MSA	None (Cooling or Evaporative Crystallizer) (Figure 12a)		Acetone (Figure 12b)		2-PrOH/DiPA (Figure 12c)
Design Variables	T_C, f_r, f_e		$T_C, f_r, x_{D,3}, x_{D,4}, x_{D,5}$		$T_C, f_r, x_{D,3}, T_D$
Key Design Equations	Production (yield) of NaCl: $P_A = F_F \left[\dfrac{\dfrac{x_{A,2}}{x_{S,2}} - \dfrac{x_{A,3}}{x_{S,3}}(1-f_e)}{\dfrac{x_{A,2}}{x_{S,2}} - \dfrac{x_{A,3}}{x_{S,3}} f_r (1-f_e)} \right]$	(8)	Additional relationship for stream 1: $\dfrac{x_{A,1}}{x_{S,1}} = \left(\dfrac{x_{A,1}}{1-x_{A,1}} \right) \left(1 + \dfrac{x_{D,5}}{x_{S,5}} f_r \right)$	(12)	
	Crystallizer sizing: $F_3 = F_F \left[\dfrac{\dfrac{1}{x_{S,3}}(1-f_e)}{\dfrac{x_{A,2}}{x_{S,2}} - \dfrac{x_{A,3}}{x_{S,3}} f_r (1-f_e)} \right]$	(9)	Production (yield) of NaCl: $P_A = F_F \left[1 - \dfrac{\dfrac{x_{A,5}}{x_{S,5}}(1-f_r)}{\dfrac{x_{A,1}}{x_{S,1}} - \dfrac{x_{A,5}}{x_{S,5}} f_r} \right]$	(13)	
	Amount of water evaporated: $F_6 = \dfrac{F_F f_e}{\dfrac{x_{A,2}}{x_{S,2}} - \dfrac{x_{A,3}}{x_{S,3}} f_r (1-f_e)}$	(10)	Crystallizer sizing: $F_3 = F_F \left[\dfrac{\dfrac{1}{x_{S,5}} \left(\dfrac{x_{D,4} - x_{D,5}}{x_{D,4} - x_{D,3}} \right)}{\dfrac{x_{A,1}}{x_{S,1}} - \dfrac{x_{A,5}}{x_{S,5}} f_r} \right]$	(14)	
	Heat requirement in crystallizer: $Q = F_3 C_{p,3}(T_C - T_{\text{ref}}) + F_6 \Delta H_v$ $- F_2 C_{p,2}(T_M - T_{\text{ref}}) - P_A \Delta H_{\text{cryst}}$	(11)	Heat requirement in crystallizer: $Q = F_3 C_{p,3}(T_C - T_{\text{ref}})$ $- F_2 C_{p,2}(T_2 - T_{\text{ref}}) - P_A \Delta H_{\text{cryst}}$	(15)	

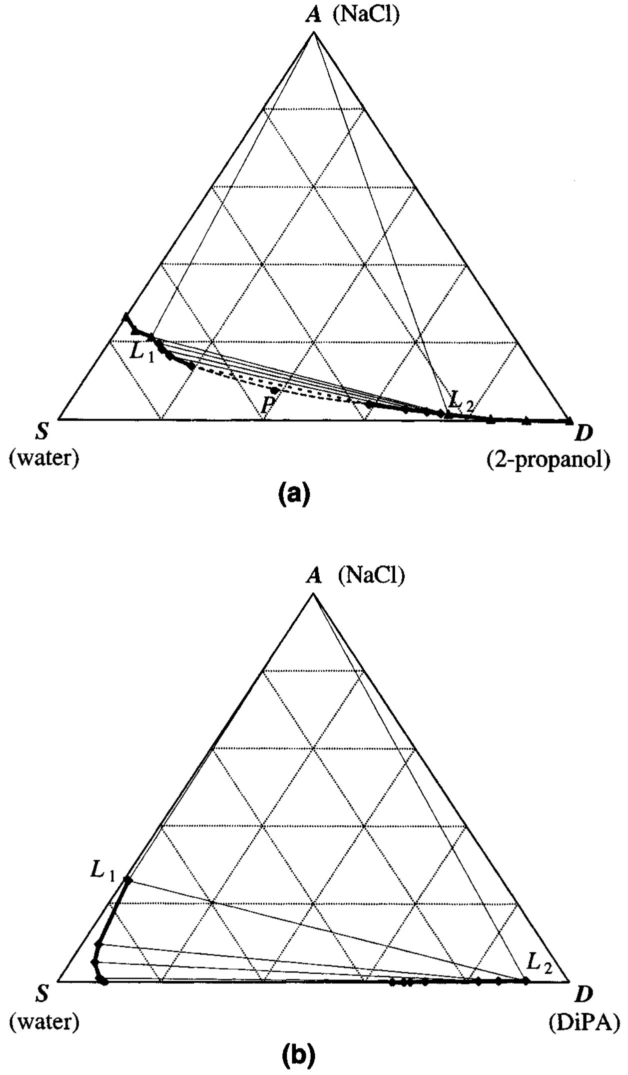


Figure 13. Isothermal phase diagrams at 25°C.

(a) NaCl–water–2-propanol (Gomis et al., 1994); (b) NaCl–water–DiPA (Davison et al., 1966).

Table 13. Design Variables and Parameters for the Production of Salt

All Alternatives	
Production rate	10 ton·h^{-1}
Effective dissolution temperature in the mine, T_M	25°C
Recycle ratio, f_r	0.99
Cooling Crystallizer Alternative	
Crystallizer temperature, T_C	1°C
Evaporative Crystallizer Alternative	
Crystallizer temperature, T_C	50°C
Drowing-Out with Acetone Alternative	
Crystallizer temperature, T_C	25°C
Distillate composition (weight fraction)	
Water	0.005
NaCl	0
Bottoms composition (weight fraction)	
Acetone	0.005
Drowning-Out with 2-Propanol Alternative	
Crystallizer temperature, T_C	0°C
Decanter temperature, T_D	25°C
Drowning Out with DiPA Alternative	
Crystallizer temperature, T_C	−5°C
Decanter temperature, T_D	25°C

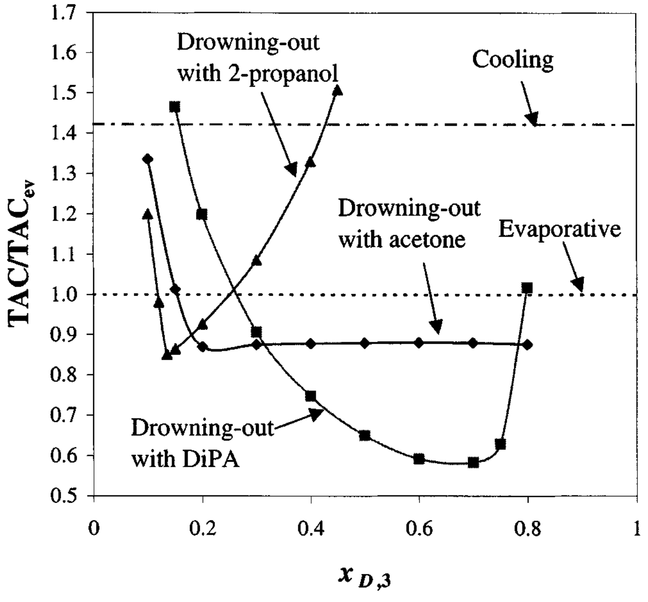


Figure 14. Comparison of five process alternatives in terms of relative Total Annualized Cost for the production of salt.

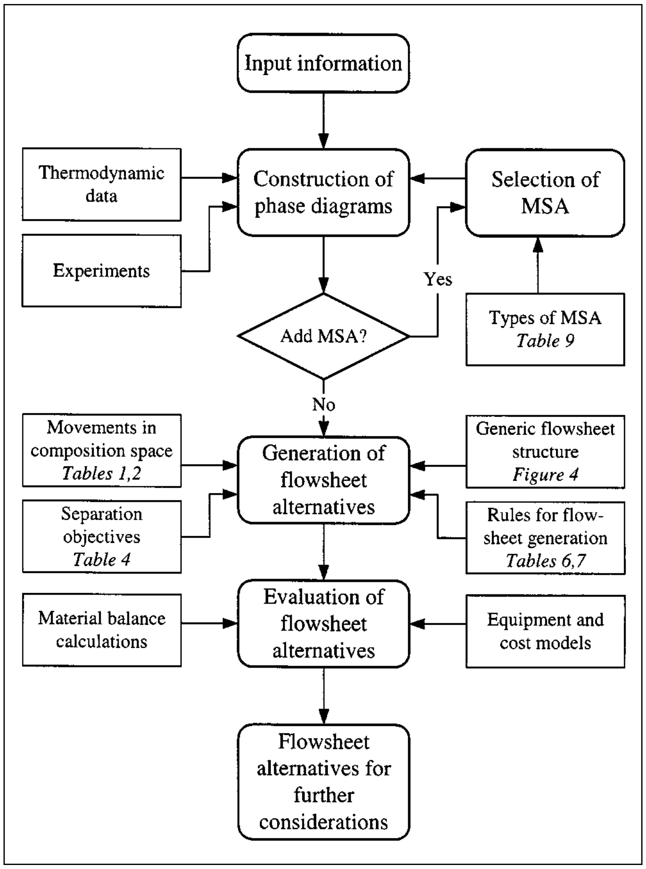


Figure 15. Summary of the unified procedure for synthesizing crystallization-based separation processes.

presented. Unlike existing design methods, this procedure is not restricted to a specific crystallization technique. Rather than providing ready-made flowsheet structures to match specific phase behaviors, it guides the user to generate flowsheet alternatives in an evolutionary manner. Depending on the separation objectives and the phase behavior of the system on hand, the resulting process alternatives may fall into one of the conventional processes or a combination of them. Flowsheet alternatives for conventional techniques presented in the literature (Dye and Ng, 1995a, b; Berry et al., 1997; Berry and Ng, 1997) can be rediscovered.

This procedure focuses on product recovery. Product qualities such as the crystal-size distribution (CSD), and kinetics and mass transport effect in crystallization (Kelkar and Ng, 1999) were not considered. The crystal products are usually sent to a series of downstream processing unit operations, such as filtration, washing, dewatering, recrystallization, and drying, where CSD plays an important role (Chang and Ng, 1998). Furthermore, it is common that the crystals are then fed into a bulk solids processing plant to produce a solids product (Wibowo and Ng, 1999). A truly optimum crystallization plant can be designed only by considering the interactions among crystallization, downstream processing, and bulk solids processing systems. Efforts in this direction are now in progress.

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Notation

$C_{p,i}$ = specific heat of stream i, $\mathrm{kJ \cdot kg^{-1} \cdot K^{-1}}$
F_i = mass-flow rate of stream i, $\mathrm{kg \cdot h^{-1}}$
ΔH_{cryst} = heat of crystallization, $\mathrm{kJ \cdot kg^{-1}}$
$\Delta H_{m,i}$ = heat of fusion of component i, $\mathrm{J \cdot mol^{-1}}$
ΔH_v = heat of vaporization, $\mathrm{kJ \cdot kg^{-1}}$
Q = heat requirement in crystallizer, $\mathrm{kJ \cdot h^{-1}}$
R = universal gas constant, = 8.314 $\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$
T_D = decanter temperature, °C or K
$T_{m,i}$ = melting point of component i, °C or K
T_{ref} = reference temperature, °C or K
x_i = mol or weight fraction of component i, dimensionless
γ_i = activity coefficient of component i, dimensionless

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Correction

In the article titled "Corrected Horvâth-Kawazoe Equations for Pore-Size Distribution" by Salil U. Rege and Ralph T. Yang (pp. 734-750, April 2000) the following corrections are made:

- On page 736, the equation for the adsorbate dispersion A_A as given by the Kirkwood-Muller formulae (Eq. 4b) was incorrectly given as:

$$A_A = \frac{3}{2} mc^2 \alpha_s \alpha_A$$

The correct formula to be used is as follows:

$$A_A = \frac{3}{2} mc^2 \alpha_A \chi_A$$

- The diameter of the nitrogen adsorbate molecule (Table 1, page 737) used in the cylindrical pore model is 3.72 Å and not 372 Å, as erroneously published.