Synthesis of Crystallization-Distillation Hybrid Separation Processes

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A systematic method to synthesize crystallization–distillation hybrid separation processes is presented. Two classes of hybrids are identified for binary mixtures. The first bypasses azeotropes and tangent pinches, while the second bypasses eutectics. Guidelines for flow-sheet selection are proposed based on an analysis of simple eutectic, constant relative volatility systems. In addition, the hybrids are compared to both extractive and adductive crystallization in order to determine the conditions under which solvent-based crystallization techniques outperform the proposed hybrid configurations. The method is extended to ternary mixture. The use of stream combination and complex distillation columns is also considered.

Introduction

Equilibrium-stage cascades can be blocked and hindered by the topology of the vapor–liquid, liquid–liquid, and solid–liquid equilibrium envelopes. For example, distillation is blocked by azeotropes and is hindered by tangent pinches in vapor–liquid composition space. Selective crystallization is prevented by eutectics and is hampered by solid solutions and temperature-insensitive solubility surfaces. The liquid–liquid immiscibility envelope determines the limiting compositions of both the extract and raffinate phases, and the magnitude of the distribution coefficient indicates the ease with which a solute is extracted. Hybrid separation processes combine two or more complementary unit operations in such a way that each unit operation is used only in regions of composition space where the unit operation is effective and economical.

Several crystallization-based hybrids have been proposed. Weingaertner et al. (1991) proposed a process that combines crystallization with extraction to solution–mine salts. Water is used to dissolve salt from the mine to form a stream saturated with salt. This stream is split. One portion is sent to the crystallizer where it is combined with an organic drowning-out agent to precipitate the salt. The mother liquor is contacted with the remaining portion of the feed in a fractional countercurrent extractor to provide a salt-lean organic-lean raffinate stream. The raffinate is stripped of remaining organic and returned to the mine. The extract is recycled to the crystallizer. This hybrid eliminates the need to vaporize excessive quantities of water, which characterizes many crystallization processes used to separate brine solutions. Berry et al. (1997) presented a systematic method to synthesize flow sheets to separate binary mixtures by crystallizer–extractor hybrids. The use of decanters, countercurrent extraction, and fractional countercurrent extraction was discussed for several phase behaviors. Gaikar and Sharma (1989) proposed separating dilute mixtures of isomers by reacting one of the isomers with solvent to form an insoluble compound. The compound is treated with an acid or base to recover the original component. An immiscible liquid can be used to further decrease the solubility of the compound. Rittner and Steiner (1985) combined melt crystallization with distillation to separate low-volatility mixtures and to bypass azeotropes.

Extractive and adductive crystallization are solvent-based techniques that require distillation columns. Usually, they are applied to high melting, close-boiling systems. Extractive crystallization uses the solvent to change the relative solubilities of the solutes to effect separations (Rajagopal et al., 1991; Dye and Ng, 1995a,b). The distillation column is used to create solvent swings and to recycle the solvent. Commercial examples include solvent dewaxing, solvent deoiling, and separation of sterols. Adductive crystallization processes use the solvent to react with one of the components in the mixture to form an insoluble compound (Berry and Ng, 1997). The compound is crystallized, filtered from the process, melted, and then distilled to recover the pure product. The other components in the mixture are usually recovered by either crystallization or distillation. In the resin-catalyzed process for the production of bisphenol A, adductive crystallization is used

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to purify the crude product (Mendiratta, 1983). Urea and thiourea complexes are also used in several commercial plants to dewax oils and to recover *n*-paraffins from heavy gas oils (Dale, 1981).

This article provides a systematic method for synthesizing crystallization–distillation hybrid separation processes. Two classes of separation are analyzed for constant relative volatility and simple eutectic systems to determine the effects of the physical properties of a mixture on the process economics. These configurations are compared with extractive and adductive crystallization to determine when the addition of a solvent is justified. Guidelines are proposed to extend the method to ternary systems.

Synthesis of Binary Separation Schemes

Crystallization–distillation hybrid separation processes offer a route to bypass thermodynamic barriers that prevent or complicate the complete recovery of products by either distillation or crystallization alone without the addition of solvents. To avoid confusion, the use of distillation alone is referred to simply as distillation, whereas distillation used in a hybrid will be referred to as the distillation step.

There are two classes of hybrids. Class I is used to bypass barriers imposed by vapor–liquid equilibrium. Class II is used to bypass barriers imposed by solid–liquid equilibrium. The physical properties and the feed composition of the mixture determines which flow-sheet structure should be considered for the separation. The process economics of the configurations within a class are compared to each other and to continuous distillation so that heuristics can be developed to select values for design variables and the most appropriate flow-sheet structure. Douglas (1988) provides the required shortcut equipment and cost models. Unless otherwise noted, the design variables for all the processes are the crystallizer temperature, and composition of the distillate, and the composition of the bottoms. Because the operating temperatures of the distillation column and crystallizers can differ significantly, the hybrid configurations should be energy integrated to reduce heat and refrigeration loads.

It will be shown that the process costs of the hybrids are sensitive to crystallization temperature, relative volatility, and feed composition. The base-case system used to compare the hybrids to distillation has a eutectic at 50 mol % *B*, but no azeotrope. Unless otherwise noted the following parameters are used. The relative volatility of *B* to *A* is 1.1. A feed composition of 80 mol % *B* and a feed flow rate of 100 kmol/h are chosen. Table 1 gives the remaining input parameters that have been chosen to be representative of intermediate to high-boiling organic compounds. Another reason for using these base-case values is that this system provides a good indicator to determine which systems are candidates for separation by a hybrid. We carried out sensitivity analysis of the results and reported them below. The process economics of the hybrid compared to continuous distillation are insensitive to ±20% changes in the values of all the input parameters given in Table 1 as long as the crystallization temperature is above 255 K. At lower temperatures the physical properties of the refrigerant can significantly impact the annualized costs.

Table 1. Input Parameters for Binary Separations

T_b	423 K
Cp_{sol}	200 J/mol·K
Cp_{ref}	110 J/mol·K
ΔH_v	36,925 J/mol
ΔH_c	13,000 J/mol
$\Delta H_{v,ref}$	16,000 J/mol

Class I separations

Class I separations bypass regions that are difficult or impossible to distill. To bypass an azeotrope, both the mole fraction of *B* at the feed ($x_{B,F}$) and at the eutectic point ($x_{B,e}$) must be either greater than or less than the mole fraction of *B* at the azeotrope ($x_{B,a}$). There are three flow-sheet configurations. Each flow sheet begins with a distillation column. The first configuration consists of a distillation-column–crystallizer equipment train. One component is recovered by distillation, the other component is recovered by crystallization. The second configuration uses distillation to provide enriched streams for the two crystallizers. Both components are crystallized. The third configuration consists of a distillation-column–crystallizer–distillation column equipment train and requires that system form either a solid solution or a compound.

Distillation–Crystallization Configuration. Figure 1 shows the distillation–crystallizer configuration. The stream numbers in the flow sheet correspond to the process points on the phase diagram. When $x_{B,F}$ and $x_{B,e}$ are both less than $x_{B,a}$,

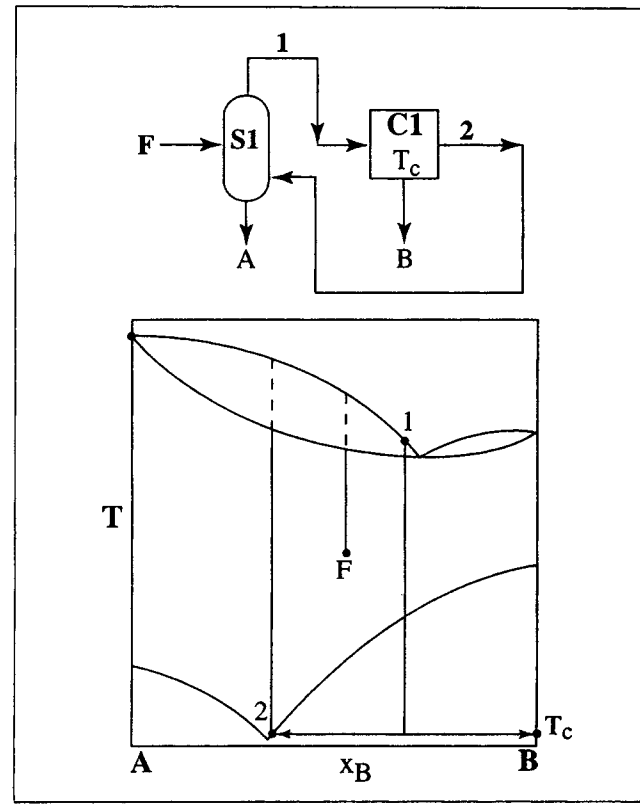

Figure 1. Class I, distillation–crystallization configuration applied to separate a mixture with a eutectic and an azeotrope.

the heavy component is recovered as the distillation column bottoms and the light component is crystallized. When $x_{B,F}$ and $x_{B,e}$ are both greater than $x_{B,a}$, the light component is recovered as the distillation-column distillate and the heavy component is crystallized.

The process to obtain the heavy component as the distillate bottoms proceeds as follows. The feed is preheated and is fed to distillation column S1. Component A is recovered as the bottoms. The stream 1, the distillate, is a mixture richer with respect to B than the eutectic point. Stream 1 is cooled and is sent to crystallizer C1, which operates at temperature T_C. This temperature should be chosen to be slightly above the eutectic temperature to provide a safety margin to prevent cocrystallization of A while providing near-maximum per-pass yield. Crystals of B are filtered and removed from the system. The mother liquor is preheated and is recycled back to the distillation column. A dual-feed distillation column can be used when the compositions of the feed and the eutectic differ significantly. Using multiple feeds can lower the reflux ratio and the number of ideal stages and thus reduce the capital cost of the process.

This hybrid process as well as other alternatives such as the use of an intermediate reboiler and condenser (Agrawal and Fidkowski, 1996) can also be applied to systems where one component is difficult to separate. For example, for the base-case system, distillation requires a reflux ratio of 18 and 180 ideal stages. The distillation–crystallization configuration requires 43% and 9% the number of stages and the vapor boilup required by distillation, respectively. The optimal distillate composition is one stage above the feed composition. Figure 2 gives the break-even curves at three crystallization temperatures as a function of feed composition. The break-even curve gives the conditions where the costs of the hybrid and distillation are equal. For example, at a T_C of 270 K and an $x_{B,F}$ of 0.1, distillation is favored when α_{BA} is above about

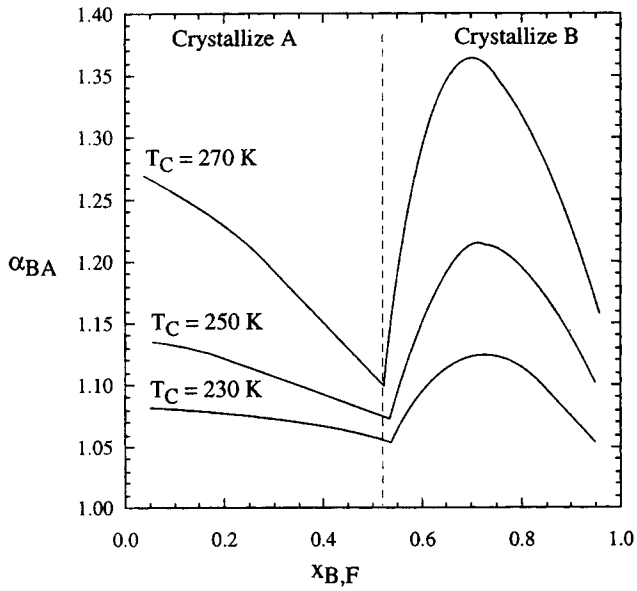

Figure 2. Process economics of Class I, distillation–crystallization configuration for base case.

1.25. Below this value, a hybrid is preferred. The shape of the break-even curve is due to two competing effects. The first effect is due to the difference between the reflux ratios of the hybrid and distillation. Lower reflux ratios reduce annual costs. The reflux ratio decreases as the difference between the composition of the distillation-column feed and distillate decreases. The hybrid requires a very low reflux ratio because the feed enters near the top tray. In contrast, the reflux for distillation must be sufficiently large so as not to create a pinch between the operating line and the equilibrium curve. The second effect arises because crystallization becomes more favorable the greater the difference between the composition of the crystallizer feed and the eutectic. This effect is most pronounced when the difference between these compositions is less than 20 to 30 mol %. Greater differences between the crystallizer feed and eutectic compositions do not create significant cost savings.

The shape of the break-even curve reflects the relative importance of cost due to reflux ratio and to crystallization. At very high concentrations of B, distillation is favored over the hybrid unless the relative volatility is very low. As the concentration of A in the feed increases, the relative performance of the hybrid to distillation improves. This is because the hybrid requires a lower reflux ratio than distillation. At approximately 70 mol % B, the curves reach a maximum. The reflux required by the hybrid continues to decrease relative to the reflux required by distillation as the concentration of A in the feed increases; however, the cost due to the crystallization step begins to increase. The hybrid process is most expensive when the feed composition is near the eutectic composition because the hybrid must use the distillation step to concentrate the crystallizer feed away from the eutectic composition. Our experience indicates that the optimal crystallizer feed concentration is about 10 to 15 mol % away from the eutectic composition. For feeds richer in A than the eutectic, A should be crystallized and B distilled. The break-even curves monotonically increase as the composition on A increases from the eutectic composition because the hybrid does not provide cost savings due to reducing the reflux ratio.

Figure 3 shows the value of the crystallization temperature at various relative volatilities to maintain a constant total annualized cost normalized by total annualized cost of continuous distillation ($TAC_{h/d}$). For the annual cost of the hybrid to match that of distillation, the relative volatility must be less than 1.7. As the crystallization temperature decreases, the relative volatility must also decrease to keep $TAC_{h/d}$ constant. At crystallization temperatures above 270 K, the costs due to refrigeration relative to the costs due to distillation are small. As the crystallization temperature drops, the costs due to refrigeration become more dominant. The annual cost of the separation is lowered by 25% and 50% if the relative volatility is 1.4 and 1.2, respectively. Notice that when the crystallization temperature is above 260 K, the hybrid can provide substantial economic improvement over distillation even for systems with relative volatilities over 1.1.

This configuration can be modified to separate a mixture that forms a solid solution. Figure 4 shows the flowsheet and a phase diagram. The only difference between this configuration and the earlier one is that a multistage crystallizer is required. Each stage operates at a different temperature. The product is obtained from the crystallizer that operates at the

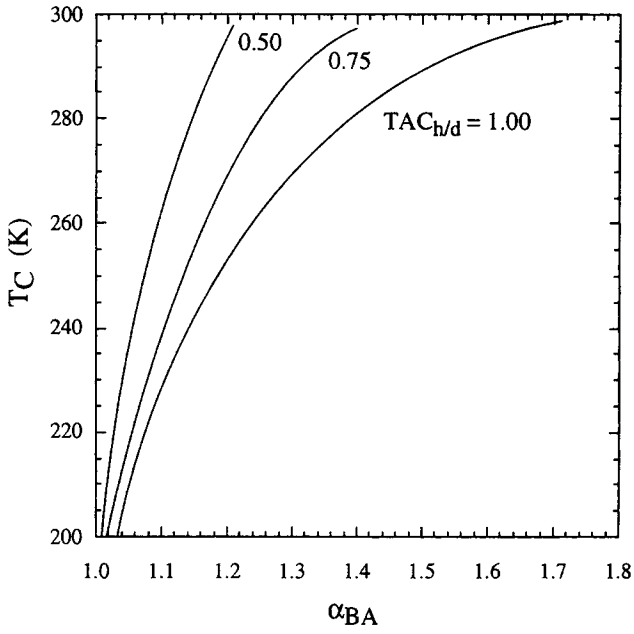

Figure 3. Constant $TAC_{h/d}$ for Class I, distillation–crystallization configuration as a function of crystallization temperature and relative volatility.

highest temperature. The mother liquor is obtained from the crystallizer operating at the lowest temperature.

Distillation–Crystallization–Crystallization Configuration. The distillation–crystallization–crystallization configuration utilizes the distillation column as a preconcentrator for two crystallizers arranged in parallel to the distillation column.

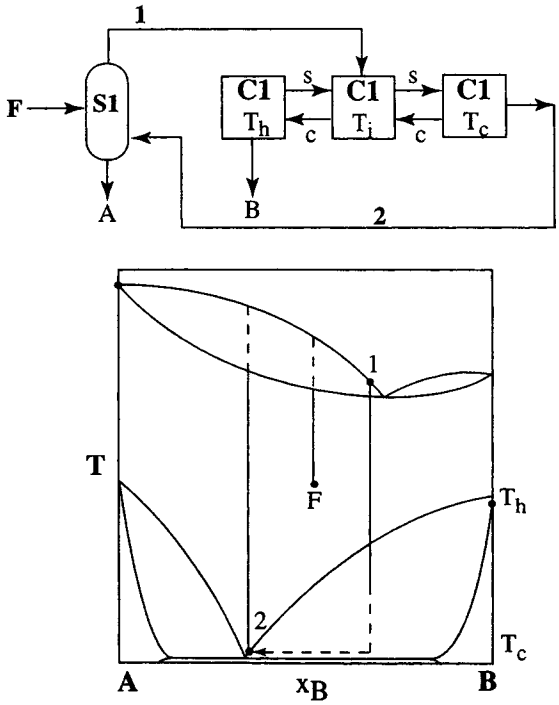

Figure 4. Class I, distillation–crystallization configuration to separate a mixture that forms a solid solution and has an azeotrope.

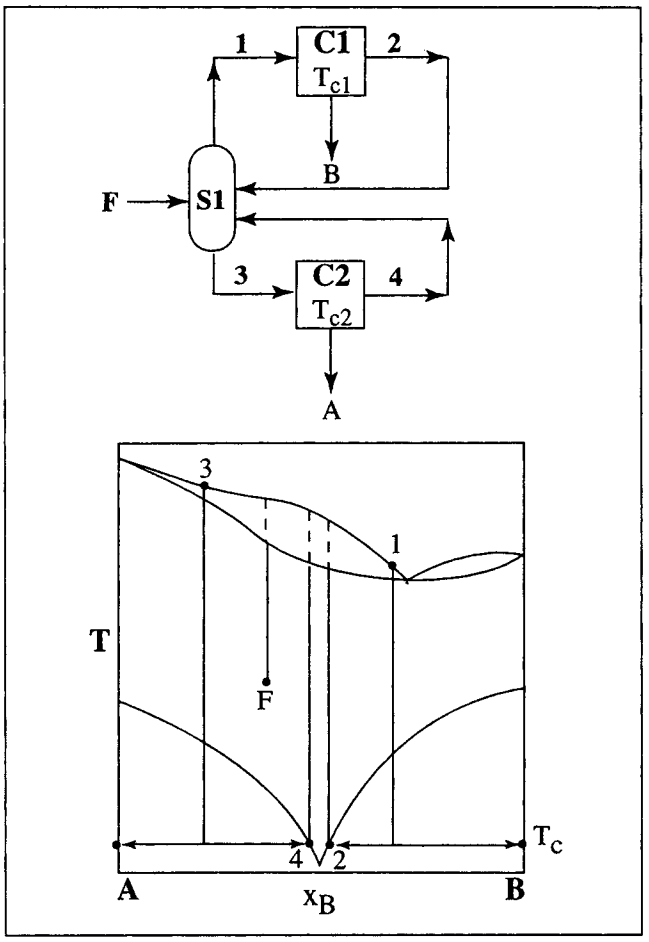

Figure 5. Class I, distillation–crystallization–crystallization configuration.

Figure 5 shows the flow sheet and the process paths drawn on a phase diagram. The process proceeds as follows. The feed is preheated and sent to the distillation column. The distillate must be more concentrated with the light component with respect to the eutectic. The bottoms must be more concentrated with the heavy component with respect to the eutectic. The distillate, stream 1, is cooled and sent to C1, which operates at T_{C1}. Component B crystallizes and is then filtered from the process. The crystallizer effluent is preheated and recycled back to the distillation column. The bottoms product is cooled and sent to C2 which operates at T_{C2}. Component A crystallizes and is then filtered from the process. The crystallizer effluent is preheated and recycled to the distillation column. This configuration can support a one-, two-, or three-feed distillation column. When the feeds to the distillation column significantly differ, each should be introduced on a different feed tray to reduce the reflux requirements. When two or more of the feeds are approximately identical, they can be combined into one stream before entering the distillation column.

For the base-case system, the hybrid requires 8 and 10% of the vapor boil-up and the number of stages required by distillation, respectively. When the feed is richer with respect to B than the eutectic, the feed is fed near the top tray of the distillation column because further enrichment is not re-

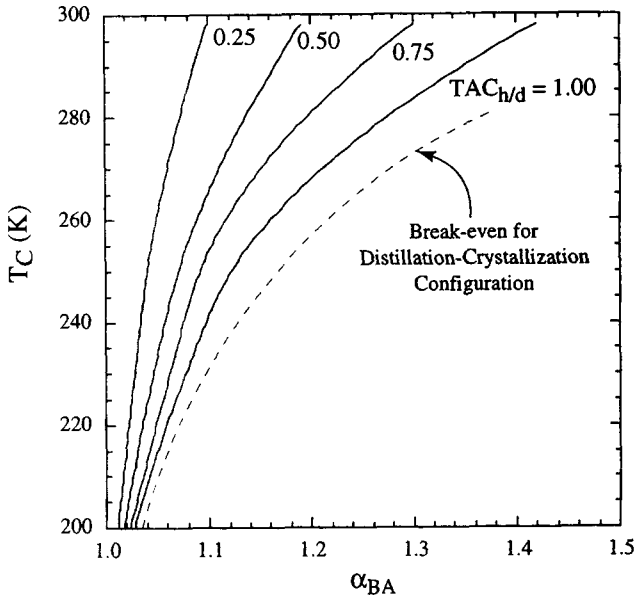

Figure 6. Curves of constant $TAC_{h/d}$ for Class I, distillation–crystallization–crystallization configuration as a function of crystallization temperature and relative volatility.

quired to crystallize B. The optimal bottoms composition is 8 mol % to 10 mol % leaner than the eutectic with respect to B. When the feed composition is leaner than the eutectic with respect to B, the distillate should range between 10 mol % and 15 mol % richer in B compared with the eutectic composition. The optimal bottoms composition is 15 mol % to 25 mol % leaner with respect to B than the eutectic.

Figure 6 shows the trade-off between relative volatility and crystallization temperature at constant $TAC_{h/d}$. For the hybrid to reduce the annual separation costs by 25, 50, and 75%, the maximum relative volatilities are 1.3, 1.2, and 1.1, respectively. For a constant relative-volatility system with a feed rich in B with respect to the eutectic, the distillation–crystallization–crystallization configuration does not perform as well as the distillation–crystallization configuration. The break-even curve for the distillation–crystallization configuration is shown by the dashed line.

Distillation – Crystallization – Distillation Configuration

The distillation–crystallization–distillation configuration is analogous to the heterogeneous azeotropic distillation flow sheets that are used to bypass a minimum boiling azeotrope; however, instead of using a liquid–liquid phase split, the hybrid utilizes a solid–liquid phase split to bypass the azeotrope and move into another distillation compartment. Each distillation column recovers one component as a bottoms product. Figure 7a applies the configuration to a system that forms a solid solution. Figure 7b applies the configuration to a system that forms a compound.

The process proceeds as follows. The feed is preheated and is sent to the distillation column. Component A is recovered as the bottoms. The composition of the distillate is near the azeotrope composition. Stream 1 is combined with the distillate from the S2 to make stream 2. The stream is cooled and

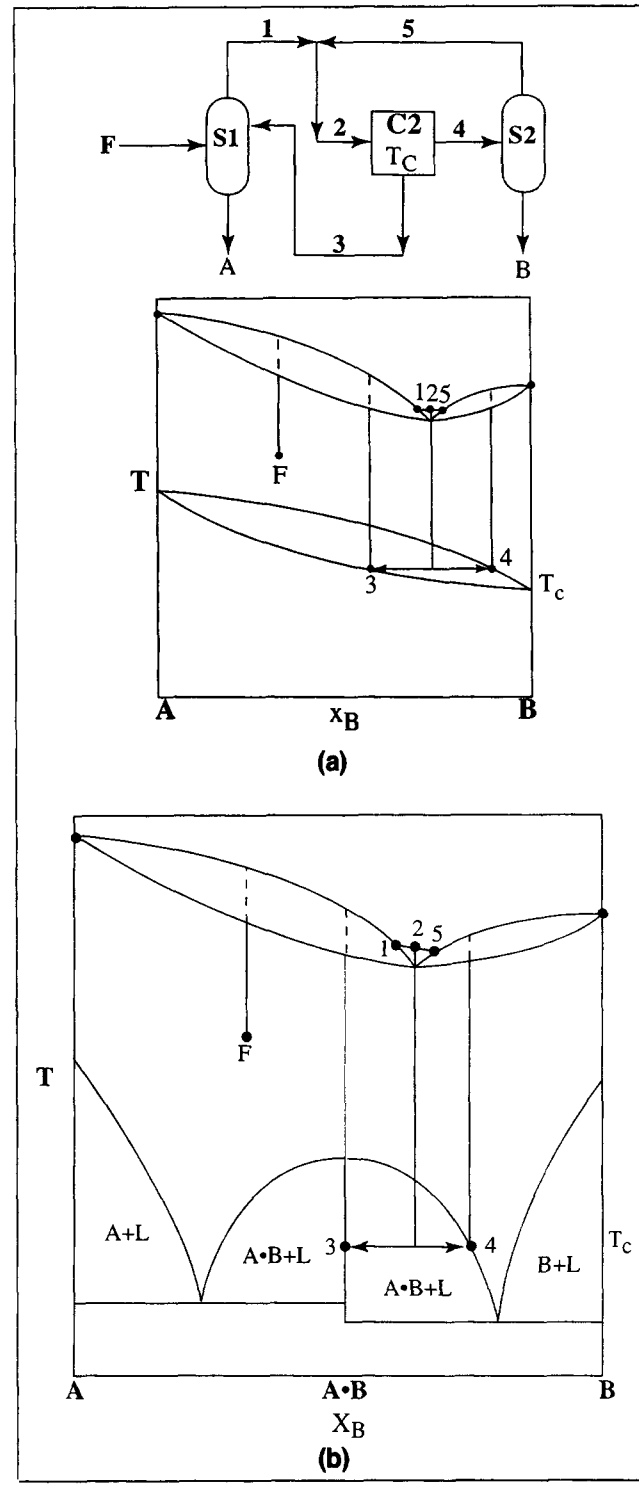

Figure 7. Class I, distillation–crystallization–distillation configuration to separate a system forming: (a) solid solution and minimum boiling azeotrope; (b) compound and minimum boiling azeotrope.

is fed to the crystallizer which operates at T_C. Crystals with a composition given by point 3 are filtered, melted, and returned to S1. When the composition of stream 3 and the feed differ, a dual-feed distillation column can be used to reduce

the reflux ratio in S1. Stream 4, the crystallizer effluent, is preheated and fed to S2. The distillate composition is near the azeotrope and is recycled to the crystallizer. Component B is recovered as the bottoms product of S2.

Class II separations

Class II separations bypass the eutectic point. To bypass a eutectic, both $x_{B,F}$ and $x_{B,a}$ must be either greater than or less than $x_{B,e}$. There are two flow-sheet configurations. Each flow sheet begins with a crystallizer. The first configuration consists of a crystallizer–distillation-column equipment train. One component is recovered by crystallization, the other component is recovered by distillation. The second configuration uses distillation to provide enriched streams to two crystallizers. In this process, both components are crystallized. Note that for a system with $x_{B,F}$ between $x_{B,a}$ and $x_{B,e}$, either Class I or Class II configurations can be used.

Crystallization–Distillation Configuration. Figure 8 shows the flow sheet for the crystallization–distillation configuration and process paths on a phase diagram. In this example, B is recovered by crystallization and A is recovered by distillation. The process proceeds as follows. The feed is combined with the distillate to make stream 1. The stream is cooled and is sent to C1, which operates at T_C. Component B crystallizes and is filtered from the system. Stream 2, the effluent, is heated and fed to S1. Component A is the bottoms product. The distillate is cooled and then recycled.

For the base-case system, the composition of the stream entering the crystallizer should be approximately 10 mol % richer than the eutectic with respect to the component to be

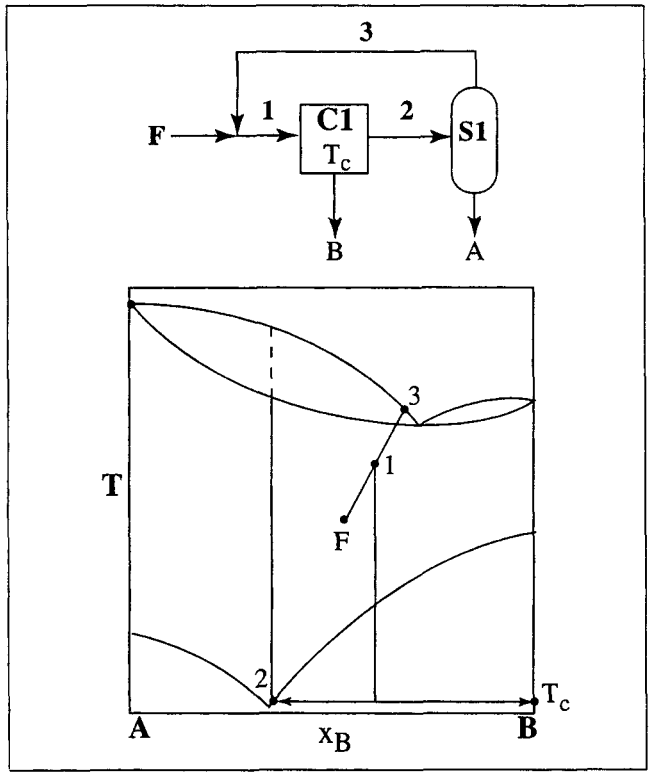

Figure 8. Class II, crystallization–distillation configuration applied to separate a mixture with a eutectic and an azeotrope.

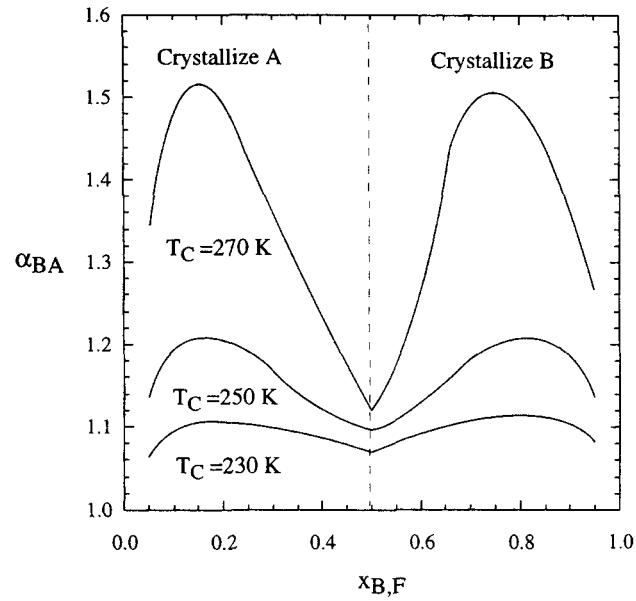

Figure 9. Process economics of Class II, crystallization–distillation configuration for base case.

crystallized. The hybrid requires 45% and 34% the vapor boilup and number of stages required by distillation, respectively.

Figure 9 shows the values of relative volatility required to break even with distillation at three temperatures as a function of the feed composition. The curves at each temperature possess maxima at $x_{B,F}$ approximately equal to 0.15 and 0.75. The hybrid is most expensive when the composition of the feed and the eutectic are equal. Component A should be crystallized for feeds composed of less than 50% B. Component A should be distilled for feeds richer in B than this composition. Regardless of which component is crystallized, the break-even curves are reasonably symmetric around the eutectic composition.

Figure 10 shows the value of the crystallization temperature at various relative volatilities to maintain a constant $TAC_{h/d}$. When the crystallization temperature is above 255 K, the hybrid process easily beats the economics of distillation, even for systems that are easy separations for distillation. Notice that the break-even curve for the hybrid increases only 5% between α_{BA} 1.4 and 2.0. When the crystallization temperature is 255 K the value of α_{BA} must equal 1.14 and 1.06 to reduce the $TAC_{h/d}$ by 75% and 50%, respectively.

Crystallization–Distillation–Crystallization Configuration. Figure 11 shows the crystallization–distillation–crystallization configuration and representative process paths. The distillation column should provide two streams on opposite sides of the eutectic point. The distillate should be 10% richer with respect to the light component than the eutectic composition. The optimal bottoms composition can range from 10% to 30% leaner with respect to the heavy component than the eutectic composition. For the base-case system, the vapor boilup and number of stages required by the hybrid is 31 and 5% that of distillation, respectively.

The process proceeds as follows. The feed is combined with the distillate. Stream 1 is cooled and then sent to the C1. At T_{C1}, B crystallizes and is filtered from the process. Stream 2

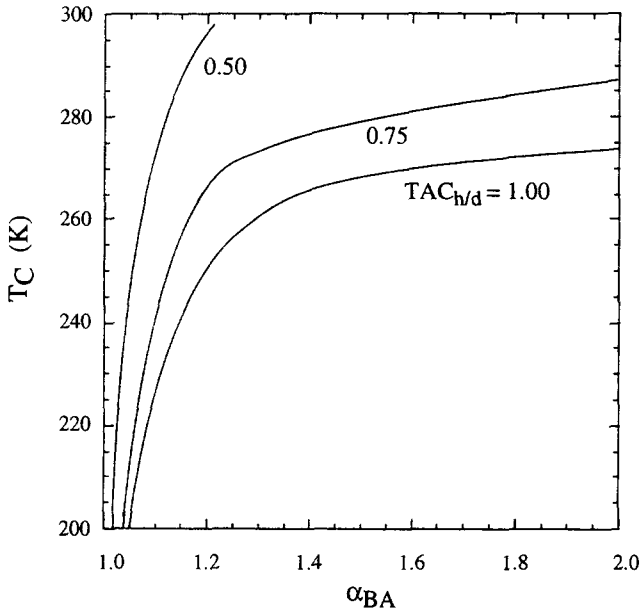

Figure 10. Constant $TAC_{h/d}$ for Class II, crystallization–distillation configuration as a function of crystallization temperature and relative volatility.

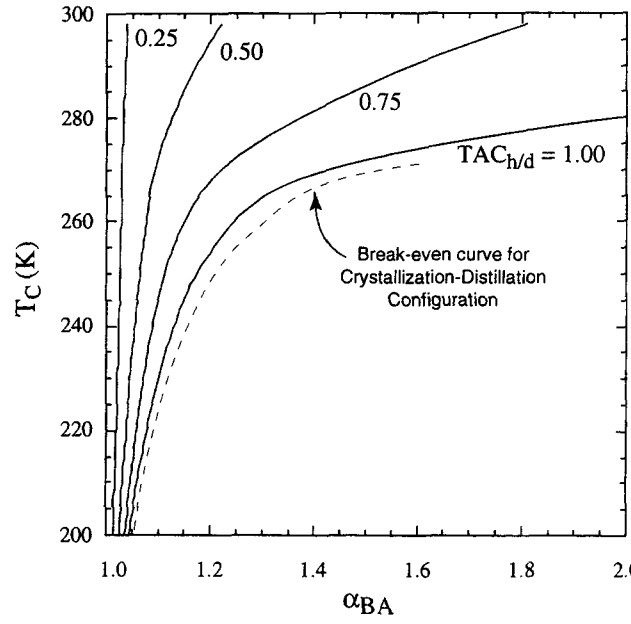

Figure 12. Constant $TAC_{h/d}$ for Class II, crystallization–distillation–crystallization configuration as a function of crystallization temperature and relative volatility.

is preheated and fed to S1. The distillate is cooled and recycled back to C1. The bottoms stream is cooled and sent to C2, which operates at T_{C2}. Component A crystallizes and is filtered from the process. The mother liquor is preheated and recycled back to S1.

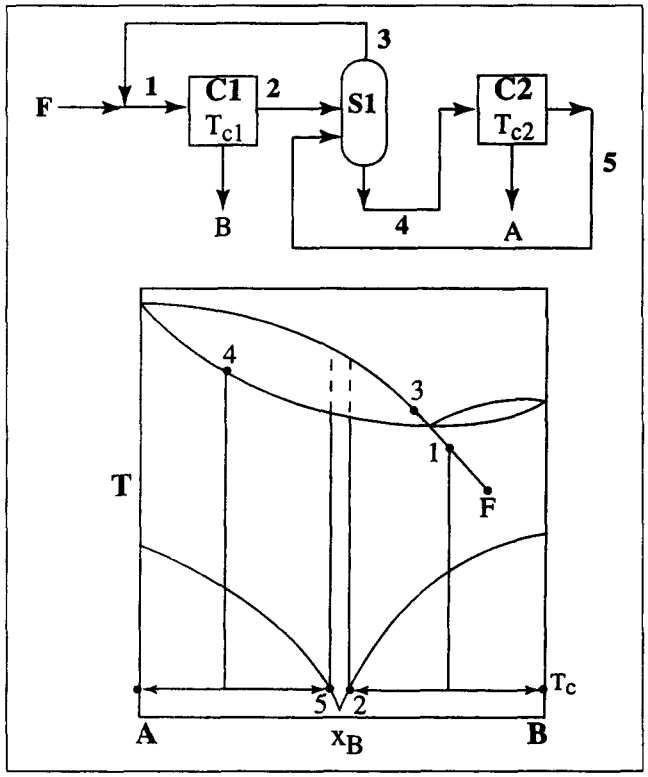

Figure 11. Class II, crystallization–distillation–crystallization configuration to separate a mixture with a simple eutectic system and an azeotrope.

Figure 12 plots the value of the crystallization temperature at various relative volatilities to maintain a constant $TAC_{h/d}$. The hybrid can compete with distillation for systems where the relative volatility is greater than 1.2 and the crystallization temperature is above 255 K. The separation costs are lowered by 25, 50, and 75% if the relative volatility is 1.8, 1.2, and 1.1, respectively.

Guidelines for Flow-sheet Selection

The boundaries for the most economical configuration can shift for several reasons. Changes in the eutectic composition will shift the boundaries because the $TAC_{h/d}$ for each configuration differs as a function of eutectic composition, feed composition, and crystallization temperature. Changes in the relative volatility with composition will also tend to change the process economics. It is expected that the best configuration is the one that uses distillation to move through regions of composition space where the relative volatility is relatively large and bypass regions of low volatility by use of crystallization.

Figure 13 compares the economics of the four configurations that can be used on simple eutectic systems. Each break-even curve represents the conditions where $TAC_{h/d}$ equals one. Break-even curves are given for T_C equal to 230, 250, and 270 K as a function of the composition of the feed. For a given temperature and feed composition, the hybrid separation is more economical than distillation when a point lies below the curve. The hybrids are most effective when the feed and the eutectic composition differ significantly. At T_C equal to 270 K the crystallization–distillation (c–d) configuration should be used for feeds as rich as 85 mol % B. The distillation–crystallization (d–c) flow sheet should be used for

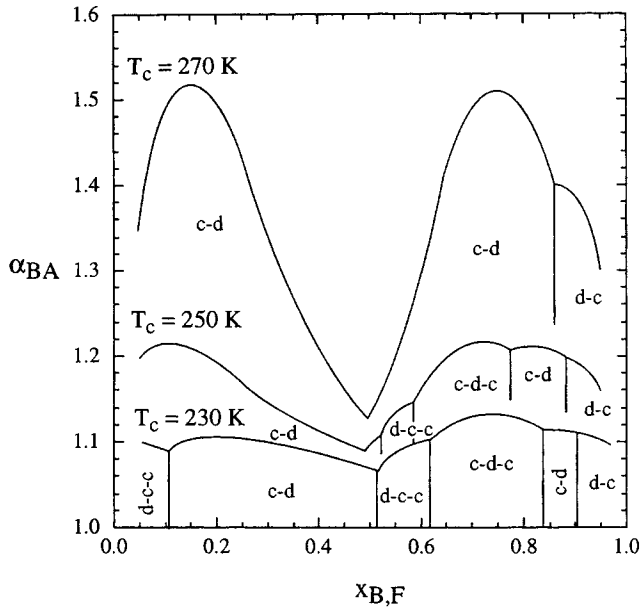

Figure 13. Comparison of all configurations for the base-case system at three crystallization temperatures.

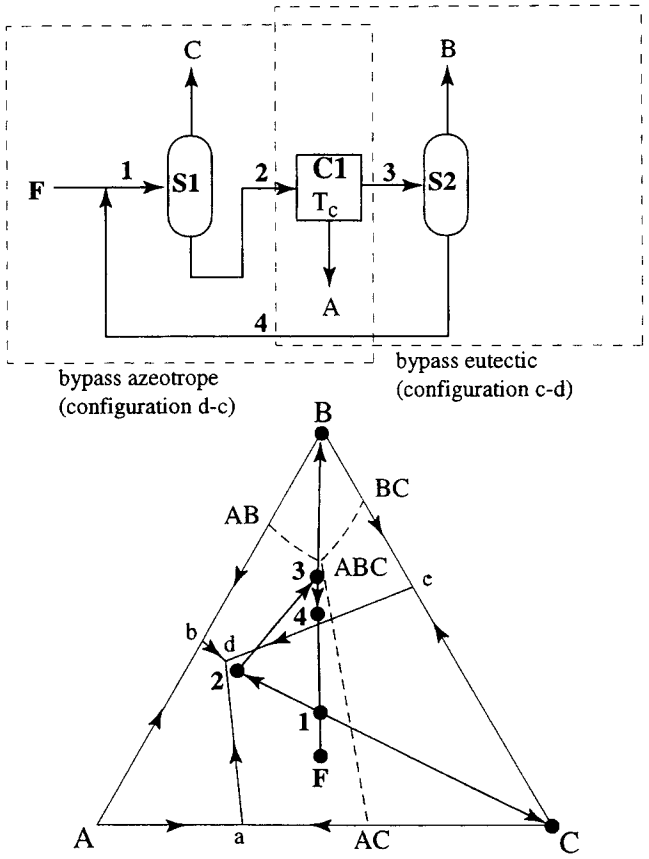

Figure 14. Separation of ternary mixture by linking the distillation–crystallization configuration to the crystallization–distillation configuration.

feeds richer with respect to *B*. As the crystallization temperature drops below 270 K, the other configurations compete better with the crystallization–distillation configuration. At T_C equal to 250 K, the distillation–crystallization–crystallization (d–c–c) configuration is most cost effective between $x_{B,F}$ equal to 51 mol % and 58 mol % *B*. The crystallization–distillation–crystallization (c–d–c) configuration is most cost effective between $x_{B,F}$ equal to 58 mol % and 78 mol % *B*. To test the applicability of the hybrid processes for a constant relative volatility system, crystallization–distillation should be considered first because the other configurations can only reduce the annual cost by at most 15%.

Synthesis of Hybrid Processes to Separate Ternary Systems

The number of process alternatives grows rapidly as the number of components in the system increase. As a starting point, the Class I and Class II schemes described in the preceding sections can be combined to separate multicomponent systems. In addition, stream combination can be used to link Class I and Class II schemes to either a crystallizer or a distillation column. Complex distillation column sequences can also be utilized.

Combining class I and class II schemes

Figure 14 shows how to separate a ternary mixture with a simple eutectic and a maximum boiling ternary azeotrope by linking the Class I, distillation–crystallization configuration with the Class II, crystallization–distillation configuration.

The polythermal solid–liquid phase diagram is represented by dashed lines. The eutectic points are given by points *AB*, *AC*, *BC*, and *ABC*. The three double saturation troughs are shown by the curves joining point *ABC* to *AB*, *AC*, and *BC*. The pure components are represented by the vertices of the phase diagram. The *A* saturation compartment is formed by the region bound by points *A*, *AB*, *ABC*, and *AC*. The *B* saturation compartment is formed by the region bound by points *B*, *BC*, *ABC*, and *AB*. The *C* saturation compartment is formed by the region bound by points *C*, *BC*, *ABC*, and *AC*. By cooling a stream within a saturation compartment, one of the pure components can be made to crystallize. Selective crystallization occurs until the composition of the solution reaches a double saturation trough. At a trough, two components crystallize and the composition of the solution moves toward the ternary eutectic point. At the ternary eutectic point a mixture of *A*, *B*, and *C* cocrystallizes.

The vapor–liquid phase diagram with distillation boundaries is represented by the solid lines. Arrows point in the direction of the heavier component. There are three distillation compartments. Component *A* can be recovered from compartment *A–a–d–b*. Component *B* can be obtained from compartment *B–b–d–c*. Component *C* can be obtained from compartment *C–c–d–a*.

The process proceeds as follows. The feed and stream 4 are combined and fed to the S1. Component *C* is recovered as the distillate. Stream 2, the bottoms, is near the ternary azeotrope composition, and the composition lies within the *A* saturation compartment. The azeotrope is bypassed by cooling the stream in C1 so that *A* solidifies. To prevent cocrystallization, the operating temperature of the crystallizer is chosen so that crystallization stops before the *AC*

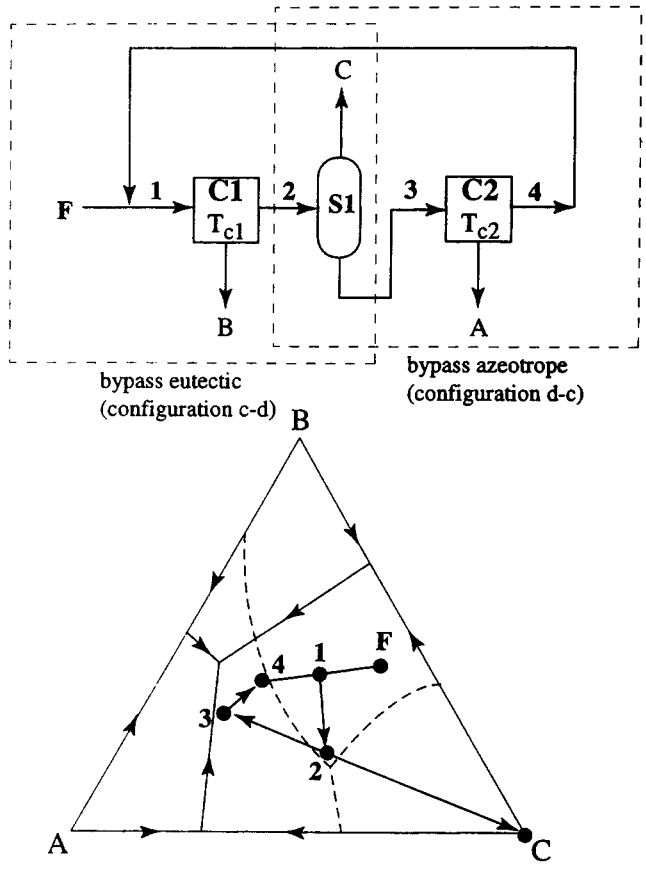

Figure 15. Separation of ternary mixture by linking the crystallization–distillation configuration to the distillation–crystallization configuration.

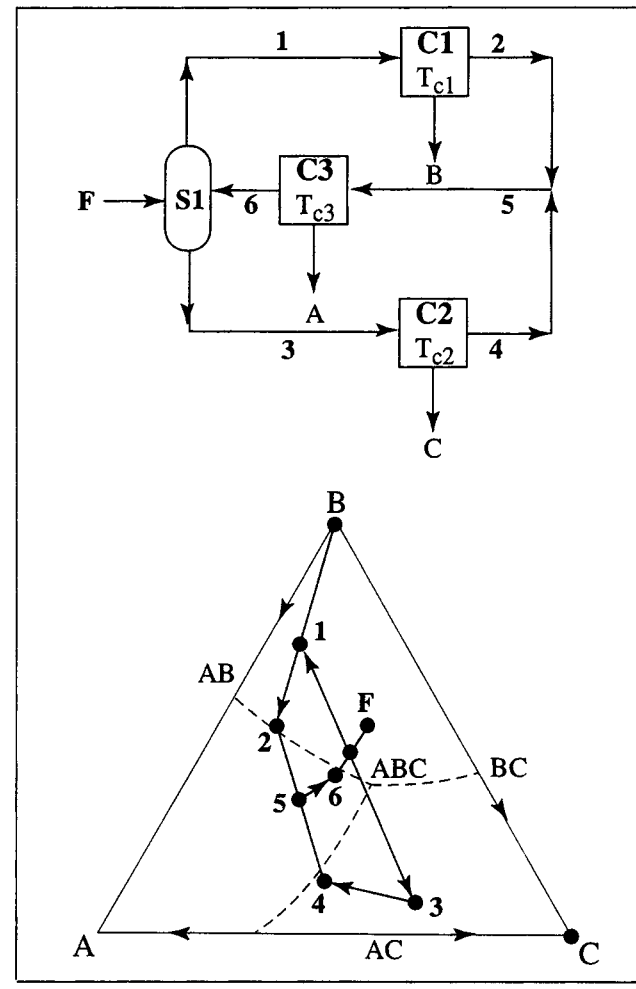

Figure 16. Use of stream combination to link an additional crystallizer to the distillation–crystallization–crystallization configuration.

double saturation trough is reached. The composition of stream 3 lies within the B distillation compartment. The double saturation trough is bypassed by distilling the mother liquor in S2. Compartment B is recovered as the distillate. The bottoms product is recycled.

Figure 15 gives an example of a flow sheet to bypass a ternary azeotrope and ternary eutectic. Component C is the light component. The distillation boundaries are marked with solid lines. The solid–liquid phase boundaries are marked with dashed lines. For the feed shown on the phase diagram either pure C or a mixture at the composition of the ternary azeotrope can be obtained by distillation alone. Notice that the composition of the ternary azeotrope lies over the A saturation surface. The process consists of a crystallizer–distillation-column–crystallizer equipment train. The process proceeds as follows. The feed and stream 4 are combined and fed to C1, where B is crystallized and filtered from the process. The effluent is fed to a distillation column. Component C is obtained as the distillate. The bottoms are fed to C2, where A is crystallized and then filtered from the process. The effluent is recycled.

Use of stream combination and an additional crystallizer

Figure 16 shows how stream combination can be used to move the system into a different saturation compartment. The process links a Class I distillation–crystallization–crystallization configuration together with an additional crystallizer. The process proceeds as follows. The feed is partially distilled. The distillate composition lies within the B saturation compartment. By sending stream 1 to C1 and by cooling to T_{C1}, B crystallizes and is filtered from the process. The bottoms composition lies within the C saturation compartment. Stream 3 is sent to C2, which operates at T_{C2}. At this temperature C crystallizes and is filtered from the process. The mother liquors from C1 and C2 are combined. The composition of stream 5 lies within the A saturation compartment. By cooling the stream to T_{C3} in C3, A is made to crystallize so that it can be filtered from the system. The mother liquor is recycled to the S1.

Use of complex distillation columns

Figure 17 shows a hybrid that utilizes a complex distillation column. The process begins by sending the feed to S1. The distillation column separates B from the mixture while providing a side stream rich in A and a bottoms product rich in C. The composition of the side stream must lie within the A saturation compartment. Upon the cooling of stream 1 in C1, A crystallizes and is filtered from the system. Stream 2 is

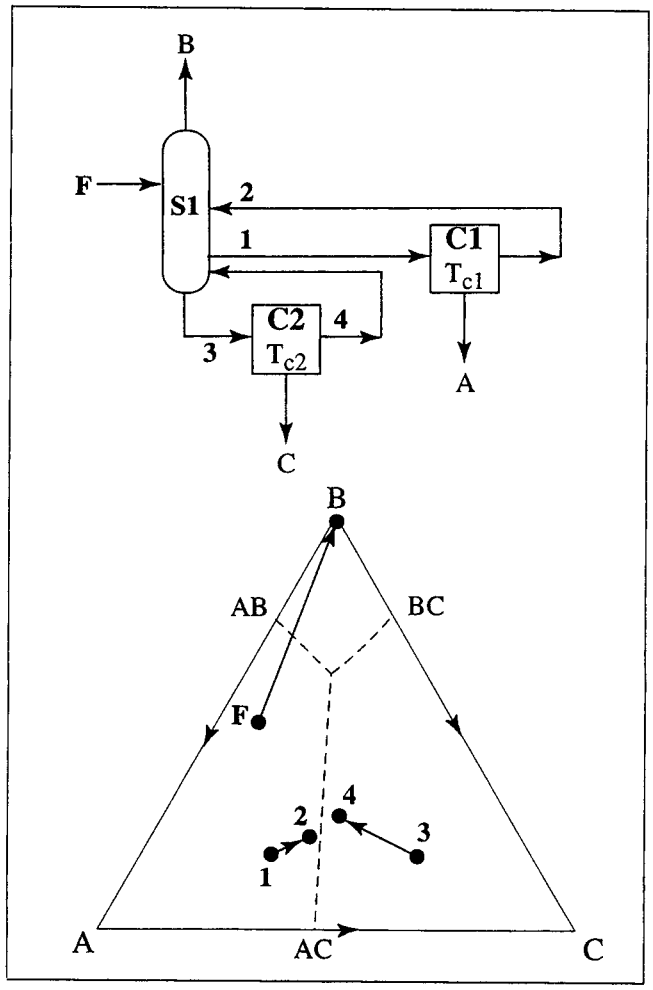

Figure 17. Hybrid configuration that uses side-stream column.

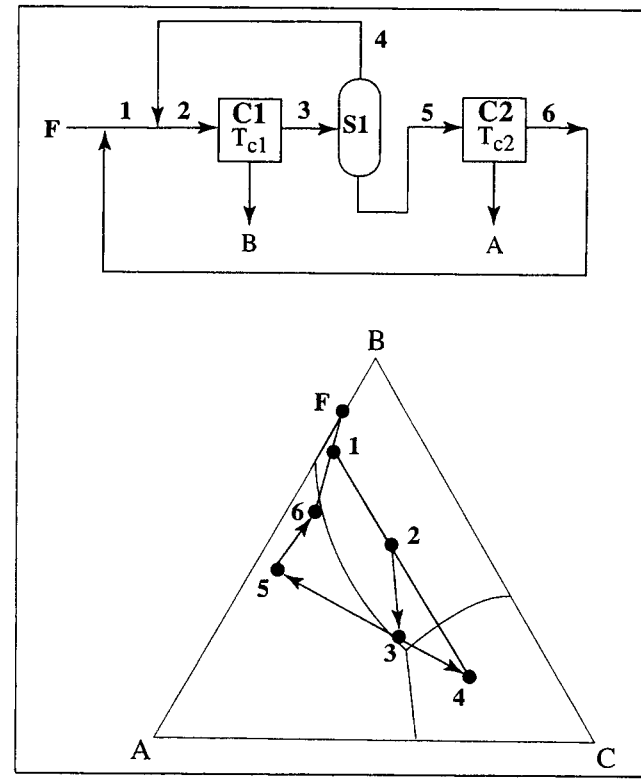

Figure 18. Separation of binary mixture by addition of solvent C.

recycled to S1. The bottoms composition must lie within the C saturation compartment. Upon cooling stream 3, C crystallizes and is filtered from the system. Stream 4 is recycled to S1.

Comparison of Hybrid Schemes to Other Crystallizaton Techniques

There are many commercial separation processes based on either extractive or adductive crystallization. Both of these techniques require an extraneous component to be added to the system to effect the separation.

Comparison to solution-based crystallization

Figure 18 shows an extractive crystallization flow sheet to crystallize B, then A. The solvent, C, is the light component. The process proceeds as follows. The feed is combined with streams 4 and 6. Stream 2 is cooled to T_{C1} to crystallize B. The effluent is fed to a distillation column. The top is rich with respect to C. The bottoms is rich with respect to the solutes. Stream 5 is sent to C2, which operates at T_{C2}. Component A crystallizes and is filtered from the system. The effluent is recycled to be combined with fresh feed.

The key feature of the phase behavior that make this separation possible is the concentration dependence of the AB double saturation trough as a function of the concentration of C. For ideal systems, the solubility is only a function of temperature, and extractive crystallization cannot be used because the relative composition of A to B at the binary eutectic is identical to that at the ternary eutectic. The solvent must also be easy to distill from the solutes. The disadvantage of using this process is that C depresses the freezing point of the solutes, thus requiring a lower crystallization temperature than the AB binary eutectic temperature. Also, because an extra component is added to the process, the equipment train must handle larger flows.

Figure 19 shows that the value of the relative volatility must be in order for it to match the performance of the Class II, crystallization–distillation configuration. For all parameter values on the plot, the hybrid beats the cost of distillation. It is assumed that the relative volatility of all the components is independent of composition. The relative composition of A:B:C at the ternary eutectic is 1:1:1. The composition of stream 3 is near the ternary eutectic. The composition of stream 6 is near the AB double saturation trough and the AB binary eutectic. It is assumed that T_{C1} and T_{C2} equal 245 and 270 K, respectively. Three systems where the AB binary eutectic is 55 mol %, 60 mol %, and 65 mol % B are considered. Given a value of α_{BA}, extractive crystallization beats the hybrid process when α_{CA} is greater than the value shown by a curve. For example, for $x_{B,F}$, $x_{B,e}$, and α_{BA} equal to 50 mol % B, 55 mol % B, and 1.06, respectively, α_{CA} must be greater than 1.75 for extractive crystallization to beat the hybrid. The relative economics of extractive crystallization to

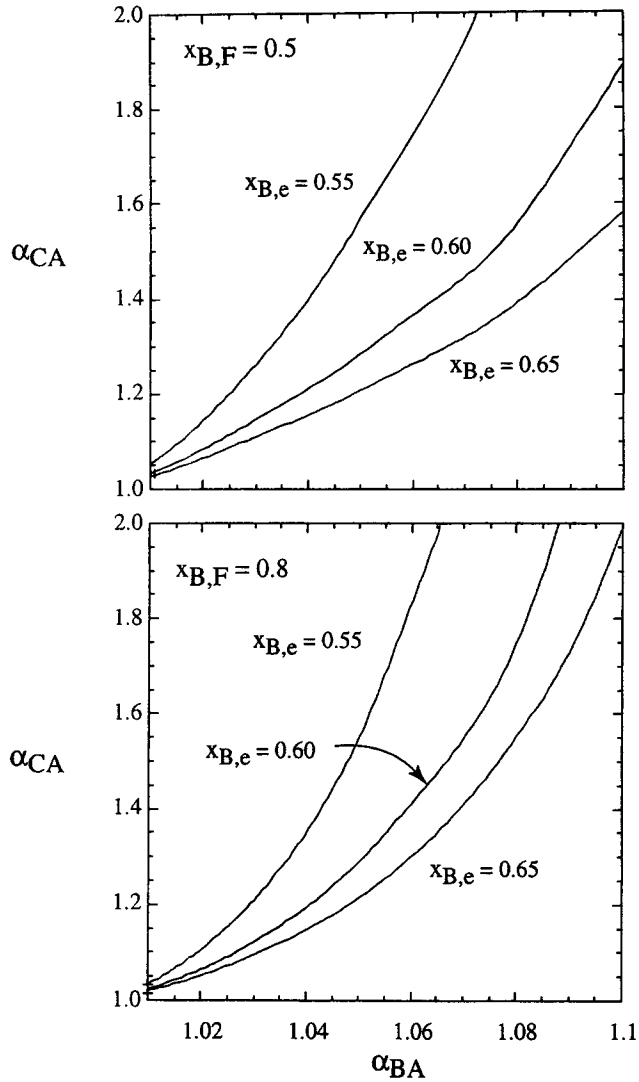

Figure 19. Comparison of solvent-based crystallization to the Class II, crystallization–distillation configuration.

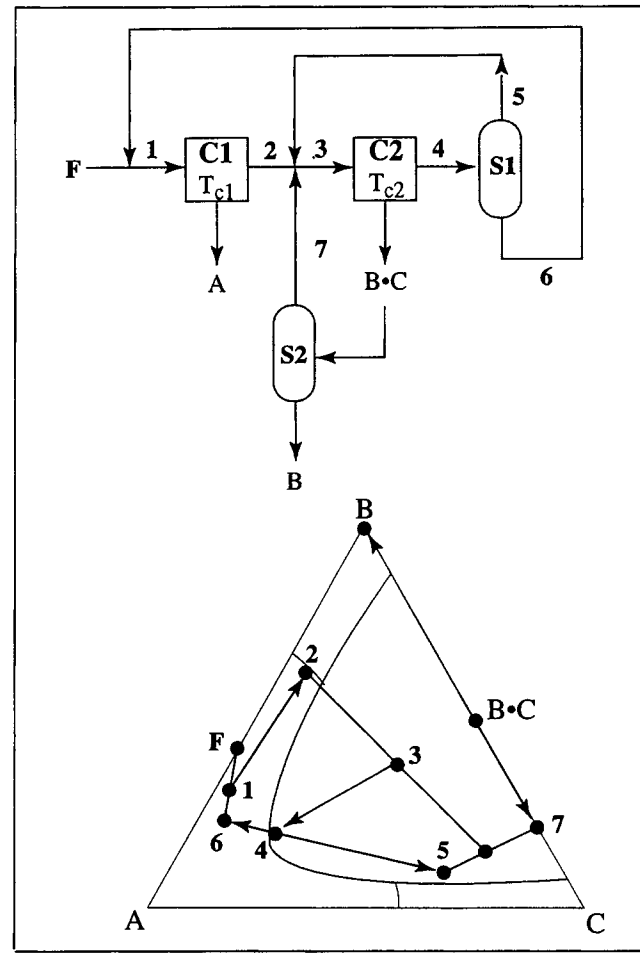

Figure 20. Separation of binary mixture by adductive crystallization.

the hybrid improves as α_{BA} decreases. This is because using a distillation step to separate A and B becomes increasingly difficult (Figure 8). The process economics of extractive crystallization also improves with the difference between the relative solubilities of A:B at the binary and ternary eutectic. Recall that the ratio of A:B at the ternary eutectic is 1:1. Like all the hybrid configurations, extractive crystallization is also most costly when the composition of the feed and the eutectic are close to one another; however, the extractive crystallization process has the best chance of beating the hybrids at these conditions. This is shown by the fact that the relative slopes of the curves for $x_{B,F}$ equal to 80 mol % B are greater than those for the respective curves for $x_{B,F}$ equal to 50 mol % B when α_{BA} is greater than 1.05.

Addition of a solvent can improve the process economics when three conditions are met. First, the solvent must easily be distilled from the solutes. Second, the value of α_{BA} is less than 1.1, preferably less than 1.05. Third, the solvent causes the relative solubility of A to B to change at least 10 mol % from that of the binary eutectic. In other words, extractive crystallization works best when distillation of the solutes is extremely expensive and the melting temperatures of the solutes is high. For intermediate value of α_{BA} between 1.05 and 2.0, one should strongly consider one of the hybrid separation configurations over extractive crystallization.

Comparison with adductive crystallization

Figure 20 is an adductive crystallization flow sheet. This process requires two crystallizers and two distillation columns. The process proceeds as follows. The feed and stream 6 are combined. Stream 1 is sent to C1, which operates at T_{C1}. Crystals of A are filtered from the process. The effluent is combined with the distillates from both distillation columns to make stream 3. This stream is sent to C2, which operates at T_{C2}. Compound $B \cdot C$ crystallizes and is filtered from the process. The effluent is sent to S1. The bottoms product is recycled to fresh feed. Crystals of compound $B \cdot C$ are remelted and sent to S2. Component B is distilled. The C-rich distillate is recycled.

Adductive crystallization processes do not rely on the solvent changing the relative solubility of A to B as do extractive crystallization processes. Instead a region on the phase diagram must form where a compound can be crystallized.

After crystallizing the compound, the relative composition of the crystallizer effluent must be significantly different from that at the binary eutectic. One advantage of this scheme is that the operating temperature of the crystallizer where the compound is obtained is not depressed as much as it would be if the solvent were inert. The disadvantages of this process are that an additional distillation column is required and crystals of the compound must be remelted. Due to the additional capital and operating costs, it is expected that adductive crystallization should only be considered when the α_{BA} is very low and a suitable solvent cannot be found for an extractive crystallization process.

Conclusions

The complementary nature of crystallization and distillation was explored in this study. The hybrids provide a route to bypass thermodynamic barriers in composition space that neither crystallization nor distillation can overcome when used separately. For a given system, the best hybrid configuration is one that uses a distillation step to move through regions of vapor–liquid composition space where the relative volatility is large and the minimum reflux ratio is low. The incentive of using a hybrid is diminished when the distillation step is used to enrich the crystallizer feed. A crystallization step is used to bypass distillation boundaries and pinches and also to reduce the column cost by providing a second feed to the distillation step.

It was shown that hybrids can economically separate binary mixtures with simple eutectics. The hybrid separations are most expensive relative to distillation when the feed is nearly pure and when the feed and eutectic have similar compositions. The hybrids can separate mixtures more effectively than distillation over a wide range of crystallization temperatures and relative volatilities. A hybrid can be chosen that utilizes the distillation step to recover one of the components or to provide feed streams to crystallizers. As the relative volatility decreases, the use of multiple crystallizers is favored. As crystallization temperature decreases, use of the distillation step to recover one of the components becomes more promising.

Another advantage of the hybrid separation processes is that they do not require the addition of solvents that can increase the process flows, create waste streams, and propagate throughout a chemical plant. Solvent-based techniques also require equipment to separate and recycle the solvent. It was found that extractive and adductive crystallization should be considered over the hybrid processes only when the solutes have very low relative volatility.

Acknowledgment

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Notation

A, B = solutes
α = relative volatility
c = crystals
s = mother liquor

Subscripts

c = crystallization
m = melting
ref = refrigerant
sol = solution
v = vaporization
w = water

Literature Cited

Agrawal, R., and Z. T. Fidkowski, "On the Use of Intermediate Reboilers in the Rectifying Section and Condensers in the Stripping Section of a Distillation Column," *Ind. Eng. Chem. Res.*, **35**, 2801 (1996).

Berry, D. A., and K. M. Ng, "Synthesis of Reactive Crystallization Processes," *AIChE J.*, **43** (7), 1737 (July, 1997).

Berry, D. A., S. R. Dye, and K. M. Ng, "Synthesis of Drowning-out Crystallization-based Separations," *AIChE J.*, **43**, 91 (1997).

Dale, G. H., "Crystallization, Extractive and Adductive," *Encycl. Chem. Process Des.*, **13**, 456 (1981).

Douglas, J. M., *Conceptual Design of Chemical Processes*, McGraw-Hill, New York (1988).

Dye, S. R., and K. M. Ng, "Bypassing Eutectics with Extractive Crystallization: Design Alternatives and Trade-Offs," *AIChE J.*, **41**, 1456 (1995a).

Dye, S. R., and K. M. Ng, "Fractional Crystallization: Design Alternatives and Trade-offs," *AIChE J.*, **41**, 2427 (1995b).

Gaikar, V. G., and M. M. Sharma, "Dissociation Extractive Crystallization," *Ind. Eng. Chem. Res.*, **26**, 1045 (1987).

Mendiratta, A. K., "Ion Exchange Catalyzed Bisphenol Process," U.S. Patent No. 4,391,997 (1983).

Rajagopal, S., K. M. Ng, and J. M. Douglas, "Design and Economic Trade-offs of Extractive Crystallization Processes," *AIChE J.*, **37**, 437 (1991).

Rittner, S., and R. Steiner, "Die Schmelzkristallisation von organischen Stoffen und ihre groβtechnische Anwendung," *Chem. Ing. Tech.*, **57**, 91 (1985).

Weingaertner, D. A., S. Lynn, and D. N. Hanson, "Extractive Crystallization of Salts from Concentrated Aqueous Solution," *Ind. Eng. Chem. Res.*, **30**, 490 (1991).

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