SEPARATIONS PROCESS SYNTHESIS

1. Introduction

Chemical process and plant design involves a hierarchy of complex and creative activities including both routine and innovative design. Routine design is largely analytical and is primarily concerned with determining values for the specification and operation of specific units, eg, reactors, extractors, and distillation columns. By contrast, process synthesis, the generation of conceptual flow sheets comprising such units, is a more open-ended activity characterized by a combinatorially large number of feasible alternatives. Finding better flow sheet alternatives has a significant impact on overall process competitiveness. This is particularly true for *separations process synthesis*, the selection of separation methods, their interconnection, and their operating parameters. Virtually every chemical process involves the recovery, isolation, or purification of products, by-products, intermediates, wastes, or raw materials. The separation systems to accomplish these tasks often dominate the capital and operating costs of chemical manufacturing processes.

Several approaches to the separations process synthesis problem have been formulated including *superstructure optimization*, *evolutionary modification*, and *systematic generation*. From a known feed composition, desired product compositions, and a well-defined set of separation methods, superstructure optimization approaches construct a hypothetical flow sheet that includes all applicable separation methods interconnected in every possible order so as to include all possible separations scheme alternatives. Separations synthesis then becomes a problem of systematically stripping away the less desirable parts of this superstructure while simultaneously optimizing the design and operating parameters of the remaining separation methods using mixed-integer nonlinear programming (1). This purely mathematical approach is computationally intensive, but is becoming well-established for certain classes of distillation synthesis problems.

Evolutionary modification starts with an existing flow sheet for a similar separation to which adaptations are made as necessary to meet the objectives of the specific case at hand. This approach is exemplified by standard flow sheet patterns, eg, the schemes for breaking heterogeneous minimum-boiling binary azeotropes or the sequences for extractive distillation (see DISTILLATION, AZEOTROPIC AND EXTRACTIVE) (2–4). Although rarely resulting in novel designs, evolutionary modification is a frequently used separations synthesis technique because of the extensive existing repertoire of design heuristics, standard patterns, and encyclopedias of complete flow sheets.

In the systematic generation approach, the separations flow sheet is constructed from a portfolio of basic components in a directed fashion so that a given feed stream is progressively transformed into one or more target compositions. This process can be viewed as the solution of integrated equipment selection, sequencing, and specification problems. Resource constraints generally limit the number of separation process alternatives that may be generated and evaluated to a small fraction of the total number of alternatives that are theoretically possible.

As a compromise between thoroughness, efficiency of evaluation, and guarantee of optimality, selection and sequencing methods often are reduced to design heuristics and simple ranked lists of physical and chemical properties characteristic of specific separation methods (5,6). This article will illustrate systematic generation separations synthesis strategies for nearly ideal liquid mixtures, as well as quite nonideal liquid mixtures. Strategies involving thermally coupled distillations and reactive separations are also presented.

2. Heuristic Distillation Sequencing for Nonazeotropic Mixtures

2.1. Synthesis Methods for Simple Distillation Systems. One practical systematic generation problem is the separation of nearly ideal liquid mixtures by simple distillation. By assuming that distillation is to be used for all separations, the separation method selection issue is eliminated. Moreover, if the liquid-phase nonidealities are not severe and the relative volatilities of the components of a liquid mixture are reasonably constant, then knowledge of the boiling points of the components provides sufficient thermodynamic information. The components are ranked in order of increasing boiling point and a split is required when two components adjacent in the ranked list, ie, keys of the separation, are desired to be in different products. Given the additional assumption of sharp separations, ie, high purity and high recovery, the distillate will consist of the light key and lower boiling components, whereas the bottoms will consist of the heavy key and higher boiling components.

Once the components are ranked by boiling point, it is a relatively straightforward task to enumerate exhaustively all possible distillation sequences. Each sequence can then be simulated in detail and the most cost-effective sequence selected by comparison. However, this search approach to separation flow sheet generation makes no use of past process knowledge nor gives any indication of the relative value of any of the sequences without significant computational effort. The use of detailed distillation simulation is a higher level of analysis than is required for screening many of the alternative sequences. Some screening can be accomplished more efficiently with heuristic-based arguments, but with the sacrifice of guaranteed optimality.

Heuristics are reliable, well-established rules for reducing the number of potential alternative sequences with minimum effort, and often lead to near optimal separation system designs. Most of the heuristics for distillation sequencing were originally formulated from parametric studies. A number of heuristics have been suggested, some of which contradict each other (7–10). A representative list follows:

Two Product Heuristic (No. 1). If there are only two products in a mixture, and all of the components in one product are more volatile than all of the components in the other product, then the next separation should divide the components into two pure products.

Process Hazard Heuristic (No. 2). If a component is corrosive, unstable, reactive, or otherwise hazardous, then the next separation should work toward removing the component from the bulk process stream.

Direct Sequence Heuristic (No. 3). If the most volatile component (product) in the mixture is greater than ~ 20 mol% of the feed, and the most volatile component (product) has the largest mole fraction in the feed, and the component (product) with the second largest mole fraction is present in a ratio of less than ~ 90% of the most volatile component (product), and the proposed separation is one of the easiest separations remaining, then the next separation should split off the most volatile component (product) as distillate.

Indirect Sequence Heuristic (No. 4). If the least volatile component (product) in the mixture is greater than ~ 20 mol% of the feed, and the least volatile component (product) has the largest mole fraction in the feed, and the component (product) with the second largest mole fraction is present in a ratio of less than ~ 90% of the least volatile component (product), and the proposed separation is one of the easiest separations remaining, then the next separation should split off the least volatile component (product) as bottoms.

Distillate to Bottoms Ratio Heuristic (No. 5). If a separation has a distillate to bottoms ratio (molar basis) of ~ 40:60–60:40, and the proposed separation is one of the easiest separations remaining, then the next separation should be the one closest to a 50:50 distillate to bottoms ratio.

Easiest Next Heuristic (No. 6). If none of the other heuristics apply, then the next separation to be done should be the easiest, that is the one with the highest separation coefficient, S, defined as

$$S = (\alpha - 1)(D/B) \quad \text{for} \quad D/B < 1$$

$$S = (\alpha - 1)(B/D) \quad \text{for} \quad D/B > 1$$

where α is the ratio of volatilities of adjacent components, D is the molar flow rate of the distillate, and B is the molar flow rate of the bottoms.

Rules for Determining Difficulty of Distillation. If $\alpha \geq 1.5$, then the given separation is one of the easiest separations remaining.

If $1.1 \leq \alpha \leq 1.5$ and there are no separations with $\alpha > 1.5$, then the given separation is one of the easiest separations remaining.

If $\alpha < 1.1$ and there are no separations with $\alpha \geq 1.1$ then the given separation is one of the easiest separations remaining.

Heuristic methods have also been extended to sequencing nonsharp distillation separations and to combinations of distillation, mixing, and stream bypass operations (11–13).

A heuristic approach is an example of an *opportunistic* systematic generation strategy. At any point in the flow-sheet synthesis procedure, the partial design generated is a feasible consequence of the initial feed composition and the separation methods so far specified. The resolution of composition differences between the intermediate streams and remaining product goals are addressed by specifying additional separation methods. No attempt is made to look ahead to anticipate or accommodate any potential difficulties in separation problem resolution. Because distillation is assumed to be feasible for all necessary separations, this opportunistic strategy will not lead to intermediate streams from which it is impossible to resolve the remaining composition differences.

2.2. Thermally Coupled Sequences.

Simple heuristic methods generate conventional distillation sequences, comprising rectifying–stripping columns each with a reboiler and a condenser, for each of $n-1$ separations. Such sequences, even when optimized can have high capital and energy-related operating costs. One method of reducing vapor traffic, potentially column diameters, number of pieces of equipment, and energy costs is to thermally couple sections of columns. A practical and widely practiced application of thermally coupled distillation sequences is the separation of air into oxygen, nitrogen, argon, and sometimes helium.

In its simplest form, thermal coupling involves using vapor from a higher pressure rectifying section to boil the underflow from a lower pressure stripping section. By using thermally coupled side stripper or rectifier sections, the vapor and liquid flows can be shared with another column section (rectifying section with a side stripper, stripping section with a side rectifier). Thus one condenser can provide the condensing duty for both the rectifying section and the side stripper. Similarly, one reboiler can provide boil-up for coupled stripping and side rectifier sections. Generalizing, only one condenser or one reboiler is required for any two column sections associated with a component of intermediate volatility.

However, there is a limit to the number of condensers and reboilers that can be exchanged for additional column sections. A condenser is always required for condensation of the most volatile component of a mixture and a reboiler for boil-up of the least volatile component. With only one condenser and reboiler, the separation of an n-component mixture into n pure products requires a minimum of $4n-6$ column sections (14).

Figure 1 illustrates three of many possible flow sheets for separating a four-component mixture, ranging from a conventional direct distillation sequence to a fully integrated one-condenser/one-reboiler configuration. The conventional sequence (Fig. 1**a**) requires 3 columns with a total of 6 column sections and 6 reboilers and condensers. The partially coupled sequence (Fig. 1**b**) has halved the number of reboilers and condensers, but increased the number of column sections to 8. The fully coupled sequence (Fig. 1**c**) requires 10 column sections with the minimum 1 reboiler and 1 condenser. Each of these configurations and the many other possible variations involve capital, energy usage, and operability trade-offs that are difficult to know *a priori*. Often highly coupled sequences suffer from difficult control issues and have seen limited application in industry. Heuristics have been proposed to help generate practical distillation sequence superstructures (14–16). The synthesis of thermally coupled distillation column sequences is a significant step up in design complexity over conventional distillation sequencing. However, sophisticated heuristic/logic and MINLP techniques are now able to solve robustly and reliably conventional to fully thermally coupled distillation sequencing problems in acceptable computation times (17,18).

3. Separations Synthesis for Nonideal Liquid Mixtures

3.1. Problem Representation. Typical liquid mixtures encountered in organic chemicals manufacturing often exhibit a wide range of melting and boiling points, reactivity, temperature sensitivity, strong thermodynamic nonidealities resulting in azeotropism, and liquid–liquid-phase formation: in general, a diverse range of behaviors that tend to complicate separation operations. A portfolio of separation methods has been developed over the years to deal with these behaviors, including, eg, simple distillation, azeotropic distillation, dual-feed extractive distillation, decantation, liquid–liquid extraction, various forms of crystallization (qv), adsorption (qv), and membrane permeation (see EXTRACTION, LIQUID–LIQUID; MEMBRANE TECHNOLOGY). Simple single-feed distillation is most widely used because of predictable, reliable, flexible, robust, and efficient operation, and because of mature equilibrium-based design techniques that do not require extensive piloting. Furthermore, simple distillation is one of the few methods that requires only the input of energy to effect the separation. Other common liquid separation methods including extraction, azeotropic distillation, extractive distillation, and solution crystallization, require the introduction of an additional mass separating agent (MSA). The MSA must then be recovered and recycled for economical operation, adding further complexity to the separations system design. The generation of separations schemes for liquid mixtures can be thought of as a problem of finding applications for distillation and the identification and resolution of situations where distillation cannot be used.

An important aspect of separations process synthesis is effective problem representation and visualization. The most widely used separation methods for liquid mixtures, including variants of distillation and extraction, are equilibrium-based processes for which the pertinent thermodynamics can be represented conveniently with graphical methods. Triangular phase diagrams (three-component systems) and tetrahedral diagrams (four components) are useful tools for visualizing separation method behavior including material balances. Useful thermodynamic representations are *residue curve maps* (RCM) and *distillation region diagrams* (DRD) for vapor–liquid equilibria (VLE), miscibility diagrams for liquid–liquid equilibria (LLE) (see DISTILLATION, AZEOTROPIC AND EXTRACTIVE; EXTRACTION, LIQUID–LIQUID), and solubility diagrams for visualizing solid–liquid equilibria (SLE) (see CRYSTALLIZATION). While these representations are useful for predicting the behavior of equilibrium-based separations, they do not predict kinetic separation methods, eg, adsorption and membrane permeation processes, although the material balances for these separation methods still can be represented graphically.

The dominance of distillation-based methods for the separation of liquid mixtures makes a number of points about RCM and DRD significant. Residue curves trace the liquid-phase composition of a simple single-stage batch stillpot as a function of time. Residue curves also approximate the liquid composition profiles in continuous staged or packed distillation columns operating at infinite reflux and reboil ratios, and are also indicative of many aspects of the behavior of continuous columns operating at practical reflux ratios (19).

The family of all residue curves that originate at one composition and terminate at another composition defines a RCM *region*. All systems with no azeotropes and even some systems with azeotropes have only one region, the entire composition space. All residue curves originate at the lowest boiling composition of the system and terminate at the highest boiling composition. However, other systems in which not all residue curves originate or terminate at the same composition have more that one region. The demarcation between regions in which adjacent residue curves originate from different compositions or terminate at different compositions is called a *separatrix*. Separatrices are related to the existence of azeotropes. In the composition space for a binary system, the separatrix is a point (azeotropic composition); for three components, the separatrix generally becomes a curved line; for four components a surface, etc.

All pure components and azeotropes in a system lie on region boundaries. Within each region, the most volatile composition (either a pure component or a minimum-boiling azeotrope and the origin of all residue curves) is the *low boiling node* (also called the *unstable node*). The least volatile composition (either a pure component or a maximum-boiling azeotrope and the terminus of all residue curves) is the *high boiling* (or *stable*) *node*. All other pure components and azeotropes are called intermediate-boiling *saddles* because no residue curves originate, terminate, or quite pass through these compositions. Adjacent regions may share nodes and saddles. Pure components and azeotropes are labeled as nodes and saddles as a result of the boiling points of all of the components and azeotropes in the system. If one component is removed from a mixture, the labeling of all remaining pure components and azeotropes, specifically those that were saddles, may change. Region-defining separatrices always originate or terminate at nodes or saddle azeotropes, but never at saddle pure components (20).

To a first approximation, the composition of the distillate and bottoms of a single-feed continuous distillation column lie on the same residue curve. Therefore, for systems with separatrices and multiple regions, distillation composition profiles are also constrained to lie in specific regions. The precise boundaries of these *distillation regions* are a function of reflux ratio, but they are closely approximated by the RCM separatrices. If a separatrix exists in a system, a corresponding *distillation boundary* will also exist. Also, mass balance constraints require that the distillate composition, the bottoms composition, and the net feed composition plotted on an RCM for any feasible distillation be collinear and spaced in relation to distillate and bottoms flows according to the well-known lever rule.

The pattern of boundaries, nodes, and saddles of a given multicomponent system is related to the boiling points of the pure components and azeotropes and is readily definable mathematically. A thorough review of the thermodynamic principles behind residue curve maps is presented by Kiva and co-workers (21). Although 125 distinct RCM or DRD are possible for three-component systems, the 14 shown in Fig. 2 are the only common maps (22). A RCM can be constructed from experimental data (for many common systems) or calculated if an equation of state or an activity coefficient expression is available (eg, Wilson parameters or UNIFAC groups). However, considerable information on system behavior can still be deduced from semiqualitative sketches based only on pure component and azeotrope boiling point data and if available approximate azeotrope compositions. This data can be used to construct DRD by the method presented in *Perry's Chemical Engineering Handbook* (2).

For a given multicomponent mixture, a single-feed distillation column can be designed with sufficient stages, reflux, and material balance control to produce a variety of different separations ranging from the *direct* mode of operation (pure low boiling node taken as distillate) to the *indirect* mode (pure high boiling node taken as bottoms). This range of operability results in a bow-tie shaped set of *reachable compositions* that may be opportunistically achieved for single-feed distillation roughly bounded by the material balance lines corresponding to the sharpest direct separation and the sharpest indirect separation possible. The exact shape of the reachable composition space is further limited by the requirement that the distillate and bottoms lie on the same residue curve, and sometimes further by peculiarities in the shape of the residue curves (23). Since residue curves are deflected by saddles, it is generally not possible to obtain a saddle product (pure component or azeotrope) from a simple single-feed column. For preliminary design purposes, the lowest and highest boiling nodes and the compositions on the distillation region boundary directly opposite the feed composition from these two nodes are of particular interest.

Figure 3 illustrates the situation for the system methylethylketone (MEK), methylisopropylketone (MIPK), and water, and the problem of recovering a pure MIPK product from such mixtures. The bow-tie approximation of reachable compositions for several feeds is shown in Fig. 3**a**; the exact reachable compositions are shown in Fig. 3**b**.

For feed F1, the upper edge of the reachable composition region is along the MEK–MIPK (water-free) face of the composition triangle and part of the lower edge is along the MEK–water (MIPK-free) face. There exist conditions under which both the water in the bottoms MIPK product can be driven to low levels (high product purity) while the MIPK in the distillate is also driven to low levels (high product recovery), although achieving such operation depends on having adequate stages and reflux ratio.

The reachable composition region for feed F2 is significantly different with the upper edge along the water–MIPK (MEK-free) face of the triangle and the lower edge along the distillation boundary. From this feed, it is not possible to achieve a high purity MIPK specification while simultaneously obtaining high MIPK recovery. If the column is operated to get high purity MIPK, the material balance line is constrained by the distillation boundary. Alternatively, if the column is operated to obtain a high recovery of MIPK (by removing the MEK–water azeotrope as the distillate), the material balance requires the bottoms to lie on the water–MIPK face of the triangle (low purity). From feed F3, which is situated in a different distillation region than the desired product, pure MIPK cannot be obtained by simple single-feed distillation at all.

Phase diagrams are particularly effective tools for separation synthesis work because of their ability to combine various types of thermodynamic information onto one representation including boiling points of pure components and azeotropes, location of azeotropes and any VLE-based distillation boundaries, location of LLE binodal curves and tie lines, melting points, eutectic points, and SLE phase compositions. Many of these thermodynamic features have a significant impact on the separation system flowsheet. Figure 4 shows examples of combined vapor–liquid and liquid–liquid phase diagrams for several ternary systems. In each of these diagrams, a number of special points, lines, and regions have been identified. Figure 4**a** shows the two-phase liquid region for the MEK–MIPK–water system previously mentioned, while Fig. 4**b** illustrates the methylene chloride–2-propanol–water system. Both systems have a distillation boundary spanned by liquid–liquid tie lines. The *n*-hexane–isopropyl alcohol (IPA)–water system is more complicated (Fig. 4**c**), exhibiting three distillation regions as well as a two-phase liquid region (24).

Relatively few points or composition regions in the phase diagram are of particular significance in separations process synthesis. These *compositions of interest* include the feed and desired product compositions, as well as azeotropes, eutectics, and selected points on liquid–liquid binodal curves. The choice of composition for a mass separation agent, if required, is critical and usually is a composition that can be conveniently regenerated in the process. Binary and ternary azeotropes that are also high or low boiling nodes (as well as the corresponding two liquid-phase compositions, if heterogeneous) are of particular interest in this regard as these points are reachable compositions by distillation and decantation. Pure components and azeotropes that are saddles are by contrast poor choices for MSA recycle as they are not included in the set of reachable compositions, unless they become nodes when another component in the system is deleted.

Although distillation is a favored separation method, quite a number of situations prevent or interfere with the use of simple direct or indirect mode distillation schemes. In general, the designer will be faced with avoiding, overcoming, or exploiting a limited set of *critical features* in order to accomplish the overall objective of the separation system. These critical features include (*1*) distillation boundaries, ie, if product (or MSA) composition is in a different distillation region from the feed mixture, the product cannot be obtained directly by simple single-feed distillation; (*2*) saddle products, ie, if a product (or MSA) is a saddle in a particular distillation region, that product cannot be obtained at high purity directly by simple single-feed distillation; (*3*) pinched or close-boiling regions, ie, if a feed and product are separated by a region of low relative volatility, simple single-feed distillation is not precluded, but tends to require a large number of stages and high reflux ratio; (*4*) overlapping melting–boiling points, ie, some solutions may contain components with melting points that are higher that the boiling points of other components and distillation of such mixtures may result in solidification within the column; (*5*) temperature-sensitive components, ie, some mixtures may contain components that degrade, decompose, polymerize, or otherwise react in an undesirable manner at the temperature conditions of distillation, thus some milder separation method must be used (25).

3.2. Flowsheet Construction. A purely opportunistic approach to separation synthesis for nonideal mixtures may again be considered. Guided by the general sequencing heuristics given, any separation method may be picked that is feasible and applicable to the state under consideration, and building the solution toward the desired products may proceed. However, the existence of the critical features mentioned previously can preclude the application of simple distillation. In systems exhibiting critical features, it is quite possible to reach an intermediate composition from which it is impossible to reduce remaining composition differences by distillation or any other separation method. The only solution is either to backtrack to an earlier intermediate composition, discarding part or all of the current flow sheet, or to follow an alternative synthesis strategy.

The purely opportunistic approach may not make use of all thermodynamic or physical property information known for the whole system. An alternative approach to separation flowsheet generation is to look ahead to potential difficulties and develop contingencies early in the synthesis process to deal with them before running into dead ends. Once a critical feature has been identified, it is useful to examine *strategic* methods for crossing, breaking, by-passing, reaching, or exploiting the critical feature. The strategies and resulting separation methods for handling a given critical feature may differ considerably and the same strategy can often be implemented in several different fashions. For example, both decantation and extraction are methods for implementing the strategy of exploiting LLE tie-lines to cross a VLE distillation boundary. Table 1 lists strategies and implementations associated with several different critical features.

Early in the synthesis of separation schemes for nonideal liquid mixtures, it may not be known exactly where in the flow sheet a strategic separation will end up, only that it will be required someplace in some form in order to overcome or exploit a particular critical feature. Thus, strategic separations often initially do not have well-defined feeds and products. The region where the feed must be located may be known, as well as a general idea of the types of products expected, but no definite compositions for either. For example, for a strategic decant operation, all that may be known initially is that the feed must be somewhere in the two-phase liquid region and the products will be on the binodal curve at opposite ends of a tie line through the feed possibly specified to be in two different distillation regions.

Along with the forward-looking strategic approach, several opportunistic separations may also be possible. These include (*1*) distill overhead the low boiling node of a mixture, with the bottoms composition constrained by mass balance and region boundary, ie, follow a direct distillation sequence; (*2*) distill the high boiling node of a mixture as underflow, ie, follow an indirect distillation sequence; (*3*) decant a two-phase liquid mixture. When critical features are present, opportunistic operations can be thought of as links between feeds, strategic separations, and products. An opportunistic operation often is used to reach a composition where a strategic separation is applicable (eg, opportunistically distill into a two-phase liquid region, then strategically decant the mixture to cross a VLE boundary). Sometimes a opportunistic separation will be equivalent to a strategic separation. Alternatively, if no critical features are present, the entire separations flow sheet can be synthesized heuristically by a series of opportunistic separations alone as discussed previously.

3.3. Separation Synthesis Algorithm. The procedure for the systematic generation of conceptual separation system flow sheets consists of the following eight steps

Step No. 1: DEFINE PROBLEM

Determine feed specifications - construct a list of all *sources* for process (source list will consist initially of all feeds).

Determine product specifications - construct a list of all *destinations* of process components (list will consist initially of compositions and amounts of all desired products and by-products to be produced by the separations process).

Determine identity of any additional species to be used as a MSA.

DECISION POINTS: Product specifications
Identity of MSA species

Step No. 2: EXAMINE EQUILIBRIUM DATA

Examine VLE, LLE, and SLE as needed.

Determine how each varies with temperature, pressure, composition, etc.

Construct a *residue curve map* (with LLE, SLE overlayed).

List *compositions of interest*. (potential MSA compositions).

Select a composition specification for the MSA (if there is an MSA). Add MSA composition to list of destinations.

DECISION POINTS: MSA composition

Step No. 3: CHOOSE A STREAM TO PROCESS

Choose a stream from the source list to process. If source list contains more than one stream, this selection may be arbitrary. All streams will eventually be processed, but order of processing may have some effect on the structure of the flowsheet synthesized.

Prepare list of known *critical features* which must be dealt with to reach all destinations (products as well as MSA compositions).

DECISION POINTS: Selection of current stream to process

Step No. 4: PROCESS STREAM

Consult Table 3 Recycle Heuristics, and Table 2 Rules for Selecting Operations. Do one of the following three things with the current stream:

1. If the composition matches that of a destination, label the stream as a product. Make note of the fact that this destination has been reached at least once.

   OR

2. Recycle the stream. Consult Table 3 for guidance.

   OR

3. Specify an operation (from the list of applicable opportunistic and strategic operations).
    (a) Determine if any of the previously identified critical features pertain to the current stream.
    (b) Examine Table 1 (corresponding to the critical features identified above), and list all strategic operations which are applicable to the current stream.
    (c) List all opportunistic separations that are applicable to the current stream (see Table 1).
    (d) Consult Table 2 to determine which strategic or opportunistic operation should be tried first.

DECISION POINTS: Selection of destination for current stream
Selection of recycle point for current stream
Selection of operation to be applied to current stream

Step No. 5: UPDATE FLOWSHEET

Connect streams.

Update flowsheet.

Add any newly created streams to source list (ie, streams resulting from separations just added to flowsheet).

Add required feed stream resulting from strategic operations just specified to destination list.

Update worksheet (stream, possible moves, chosen move, decision point).

DECISION POINTS: NONE

Step No. 6: OTHER STREAMS TO PROCESS?

If the source list is not empty, then the flowsheet is not complete. Additional streams must be processed.

RETURN TO STEP No. 3

Step No. 7: ALL PRODUCT (INCLUDING MSA AND STRATEGIC OPERATION FEED) SPECS MET?

The solution is complete if all product specifications have been met.

If the flowsheet cannot meet the product specs as originally stated. Determine if they can be “relaxed” - are the products specs that can be obtained with the current flowsheet actually satisfactory? If yes, then the solution is complete.

DECISION POINTS: All problem specs met?

Step No. 8: GENERATE ALTERNATIVE SOLUTIONS

Once an acceptable flowsheet has been generated, consider evolutionary modification.

If another solution is desired, then return to any/all of the decision points and choose different alternatives.

The synthesis scheme emphasizes the use of the appropriate knowledge, identification of critical features and strategies to deal with them, and provides a means for selecting and sequencing both opportunistic and strategic separations. The process begins by the construction of lists of *sources* and *destinations* for the process. A source may be the original feed mixture or a stream created by a strategic or opportunistic separation. A *source list* is maintained as the algorithm progresses. It contains streams that have not been identified as destinations, have not been recycled, nor fed into another unit operation. Destinations are the final and sometimes intermediate objectives of the separation flow sheet. They may be products, by-products, MSA compositions that must be regenerated and recycled, or the feed to a strategic separation. The destination list also changes as the design proceeds.

The thermodynamics and physical properties of the mixture to be separated are examined. VLE nodes and saddles, LLE binodal curves, etc, are labeled. Critical features and compositions of interest are identified. A stream is selected from the source list. This stream is either identified as meeting all the composition objectives of a destination, or else as in need of further processing. Once an opportunistic or strategic operation is selected and incorporated into the flowsheet, any new sources or destinations are added to the respective lists. If a strategic separation for dealing with a particular critical feature has been implemented, then that critical feature is no longer of concern. Alternatively, additional critical features may arise through the addition of new components such as a MSA. The process is repeated until the source list is empty and all destination specifications have been satisfied.

Separation method selection is governed by a two-tier set of rules in Table 2. The first tier involves the selection between strategic and opportunistic operations. Strategic separations are favored, as these are known to be required in the flowsheet at some point, as are separations that directly reach a desired product composition. The second tier uses the same general sequencing heuristics outlined previously to help guide the process toward lower cost sequences when more than one alternative is feasible.

The recycling of a stream to a point upstream in the process is often a powerful alternative to performing additional processing. In particular, regeneration and recycle of an MSA composition is essential to the economic operation of such separation methods as extraction, extractive distillation, and azeotropic distillation. However, recycling cannot be done indiscriminately and material balances must be carefully considered. Unit operations that worked before closing the recycle may no longer function in the same manner, or may become infeasible. For example, the recycle may cause an upstream composition to move into another distillation region making a previously specified distillation now impossible. Alternatively, the recycle may result in the infinite build-up of a particular component if there is no outlet for that component from the recycle loop. Table 3 presents recycle heuristics for guidance.

3.4. Separation Selection Issues. Separations process synthesis is an open-ended design activity. Often very distinct flow sheets can be generated if the choice of MSA is changed, a different separation method is applied to a particular stream, or even by changing the order in which streams on the source list are examined. Such *decision points* are found throughout the algorithm and are the mechanism for generating alternative flow sheets. Each decision point can be revisited, another alternative selected, and the section of the flow sheet resulting from this decision point can be revised. Potential decision points for each step of the algorithm are noted in the Section 3.3.

It is particularly difficult to give rules for finding the "best" separation method among several feasible alternatives for nonideal mixtures. Ranked lists of physical properties may not have enough discriminating power without resorting to more in-depth calculations. However, knowledge of a few properties characteristic of each separation often can help eliminate feasible, but poor choices, as well as indicate better alternatives clearly. Table 4 lists pure component and mixture properties that characterize several liquid separation methods. Sections 3.4.1–3.4.3 present a list of general separation heuristics for distillation-based separation methods, crystallization methods, and other methods requiring an MSA. Sources of information on MSA selection is included in the list of references in the tables.

I. General Separation Heuristics: Distillation-Based Methods

1. *Distillation* (2,26,27)
   (a) Usually cannot be beaten when α (relative volatility) ≥ 1.5. Competitive for $1.1 \leq \alpha \leq 1.5$. Other methods usually better for $\alpha \leq 1.05$ to 1.1.
   (b) Becomes difficult (likely to require large number of stages or reflux) when temperatures of high boiling and low boiling nodes of region differ by $< 10°C$.
   (c) Very difficult when temperatures of high and low boiling nodes of region differ by $< 5°C$.
   (d) Simple one-column distillation is generally unfavorable when the bottoms to distillate ratio is either very high or very low (eg, $95/5 \leq D/B$ ratio $\geq 5/95$). For low D/B ratio high reflux required. For high D/B ratio large amount of feed must be vaporized.
   (e) Consider special multiple-effect distillation schemes if the bottoms to distillate ratio is either very high or very low, or if the relative volatility is low.
   (f) Avoid attempts to recover simultaneously both high and low boiling nodes in high purity from mixtures of three or more components, particularly in columns that reflux compositions different from the distillate composition (ie, reflux of one phase from a decanter), as such operation may be difficult to control.

2. *Azeotropic Distillation* (2) (see DISTILLATION, AZEOTROPIC AND EXTRACTIVE)
    - (a) The more structurally, chemically similar components are, the less likely that the separation will be improved by azeotropic distillation (if an MSA-key component azeotrope is being used to alter the RCM). Any azeotropes formed between one component and another similar component will tend to have similar boiling points, compositions.
    - (b) MSA selection is critical.
    - (c) See 8a1-6 above.

3. *Extractive Distillation* (2) (see DISTILLATION, AZEOTROPIC AND EXTRACTIVE)
    - (a) Usually not favorable for separation of components that show very similar liquid-phase behavior: steroisomers, homologous series, isonormal–neoisomers. Components to be separated must have some different functional group for MSA to affect liquid-phase behavior differentially.
    - (b) Only certain residue curve maps are favorable for extractive distillation.
    - (c) MSA selection is critical.

4. *Pressure Swing Distillation* (2,26) (see DISTILLATION, AZEOTROPIC AND EXTRACTIVE)
    - (a) Azeotrope composition must change at least 5–10 mol% over moderate pressure change for process to be economical. Generally larger change required for minimum boiling azeotrope than maximum boiling azeotrope. Extent of pressure change somewhat dictated by reboiler temperature in high pressure column, condensing temperature in low pressure column (try to avoid refrigeration, special heat exchange fluids).
    - (b) For minimum boiling azeotrope, generally less favorable because recycle composition between columns taken overhead, pure products are bottoms: results in high energy usage, larger column size, products will contain any high boiling contaminants.
    - (c) For maximum boiling azeotrope, generally more favorable because recycle composition between columns are bottoms streams, pure products are distillates: recycle not as energy-intensive, products are distilled once.

5. *Distillation into Curved Boundary* (2) (see DISTILLATION, AZEOTROPIC AND EXTRACTIVE)
    - (a) More curved the boundary, the less recycle required. Generally less favorable for minimum boiling azeotropes due to large overhead recycles.
    - (b) Consider other methods if recycle rates are high (ie, three to five times feed rate or more).
    - (c) Boundaries involving maximum azeotropes often highly curved.
    - (d) Not applicable to binary systems; azeotrope is point in phase diagram.

6. *High Vacuum Distillation* (28,29)
    - (a) Consider high vacuum distillation when material is temperature sensitive at normal pressure ranges.
    - (b) Consider wiped-film evaporator (external condenser) when pressure must be in 5–0.1-Torr range.

(c) Consider short-path evaporator (internal condenser) when pressure must be in 0.1–0.001-Torr range. For larger scale production, 0.01–0.005 Torr is practical lower pressure limit.
(d) At best, only one equilibrium stage achievable for each WFE or SPE unit. Separation efficiency decreases as pressure decreases.
(e) Operate at a vacuum no lower than required. Short-path unit typically 25–35% higher cost than wiped-film unit.
(f) Separate all noncondensables before feeding to WFE or SPE unit. Even a small amount of noncondensables will overload vacuum system, especially at ultrahigh vacuum ranges. Remember that most low molecular weight compounds will not condense at cooling water temperatures under high vacuum.

II. General Separation Heuristics: Crystallization Methods (30–32)

1. *Solution Crystallization: General*
   (a) Cost increases greatly with decreasing temperature. Try to keep at or above 0–20°C.
   (b) Order of preference: adiabatic evaporation $>$ evaporation $>$ cooling $>$ drown-out.
   (c) If system forms solid solution then multistage crystallization required. Likely to be expensive option.

2. *Solution Crystallization: Adiabatic Evaporation (Vacuum Cooling)*
   (a) Favored for systems where temperature change has moderate effect on solubility.
   (b) Generally best when crystallizing component is 20–75% of feed mixture.
   (c) Solvent must have sufficient volatility to be easily removed at target temperature and vacuum levels.
   (d) May be inferior for systems with high boiling point elevations (high vacuum levels required).
   (e) Components must be stable at flash point of mixture. Will probably run under vacuum. Vacuum $<$ 50–100 Torr may require specialized (scraped-film) crystallizer, more complicated vacuum system.
   (f) If running under vacuum, separate noncondensables before feeding to crystallizer. Excessive noncondensables will overload vacuum system or lead to oversized design.
   (g) Complete recovery possible in theory. In practice recovery dictated by solubility limit of impurities and viscosity of solution.

3. *Solution Crystallization: Isothermal Evaporation*
   (a) Favored for systems where solubility has little temperature dependence. Can be used in other cases.
   (b) Solvent to be evaporated must have high volatility compared to remainder of solution.

(c) Theoretical yield is 100%, but usually limited by cocrystallization of impurities.

(d) Use single effect if crystallizing component is greater than $\sim 75\%$ of feed.

(e) Consider multiple effects if crystallizing component is $< 75\%$ of feed.

(f) Can be very energy intensive. Energy usage per pound of product highly dependent on heat of vaporization of solvent and number of effects used.

(g) Components must be stable at boiling point of mixture. May have to run under vacuum. Vacuum $< 50-100$ Torr may require specialized (scraped-film) crystallizer, more complicated vacuum system.

(h) If running under vacuum, separate noncondensables before feeding to crystallizer. Excessive noncondensables will overload vacuum system or lead to oversized design.

(i) Complete recovery possible in theory. In practice, recovery dictated by solubility limit of impurities and viscosity of solution.

4. *Solution Crystallization: Cooling*
   (a) Generally best when crystallizing component is 20–75% of feed mixture.
   (b) Solubility should be strong function of temperature. Solubility should decrease with decreasing temperature.
   (c) Feed should be close to saturation limit before cooling to maximize potential recovery. May consider preconcentration step to remove excess solvent.
   (d) Recovery limited by eutectics.

5. *Solution Crystallization: Drown-Out or Salt-Out*
   (a) Consider when solvent cannot be removed by evaporation (either temperature sensitivity or low solvent volatility).
   (b) For drown-out, look for MSA in which the component to be crystallized has low solubility, while other components have high solubility. MSA should be completely miscible with feed mixture.
   (c) For salt-out, add solute that reduces effective solubility of component to be crystallized. Salt with common ion usual choice. Salting-out compound should be cheap, as may be difficult to recover.
   (d) Generally best when crystallizing component is large percentage of feed. Consider preconcentration step if dilute.

6. *Melt Crystallization*
   (a) Mixture must be stable at temperatures 20°C above melting point of crystallizing component.
   (b) Crystallizing component should be at least 50% of feed mixture, preferably 75% or more.
   (c) Melting points must be between -30 and 150°C for practical implementation.
   (d) Crystallizing component should show sharp melting point.
   (e) Metastable zone width should be $< 25°\mathrm{C}$ for efficient crystallization.

- (f) Large difference in melting point and eutectic temperature improves controllability.
- (g) Difference of 20–30°C between melting points of pure components more favorable.
- (h) Recovery limited by eutectics.
- (i) Cost increases greatly with decreasing temperature. Try to keep at or > 0–20°C.

III. General Separation Heuristics: Other Methods Requiring MSA

1. *Stripping (steam)* (33)
    - (a) Particularly good for components that form minimum boiling azeotropes with water and are immiscible with water: tend to have extremely high volatilities.
    - (b) Not good for low boilers that are completely miscible with water (eg, methanol, acetone).
    - (c) Generally uneconomical if component to be stripped is > 10–15% of feed mixture (too much steam required). Should use other methods to remove bulk of component.
    - (d) Be prepared to expect some product contamination if feed components can react with water (eg, ester will be partially hydrolyzed to acid and alcohol). Fate of reaction product species will depend on above rules (eg, methanol from methyl ester hydrolysis probably will not be stripped out of bottoms stream).

2. *Extraction* (26,34,35) (see EXTRACTION, LIQUID–LIQUID)
    - (a) Usually not favorable for separation of components that show very similar liquid-phase behavior.
    - (b) MSA selection is critical.
    - (c) Consider component already in mixture for MSA if system exhibits appropriate liquid–liquid behavior.
    - (d) For given binary pair two-phase behavior likely when infinite dilution activity coefficient of either component in other component is greater than or equal to ~ 7.5.
    - (e) For trace removals (eg, catalyst recovery) usually can get to < 100 ppm, but not much lower. Often difficult to regenerate solvent to such low levels.

3. *Adsorption (liquid phase)* (26)
    - (a) Species can only be separated by molecular sieving effects when their kinetic diameters fall into different zeolite aperture size categories. Standard molecular sieve diameters are nominally 3, 4, 5, 8, 10, 13 Å.
    - (b) Dehydration of organics (removal of $<1\%$ water) generally feasible by molecular sieving, if kinetic diameter of organic > 3 Å.
    - (c) Selectivity generally unfavorable when system components are miscible in all proportions (may not be a problem when removal is the objective).

(d) Sparingly soluble minor components are more favorably adsorbed.
(e) Strong hydrogen bonding of component with like or unlike molecules tends to retard adsorption.
(f) Only for dilute solutions ($< 1-2\%$ of feed), unless molecular sieving effect also present.
(g) Activated carbon adsorption generally uneconomical for removal of > 1000 ppm contaminant from large stream unless willing and able to regenerate bed. Steaming often easiest regeneration method, but creates new waste water problem. Usually 3–5-lb steam required per pound of carbon for regeneration.
(h) Do not regenerate molecular sieves by steaming. Water typically is very strongly adsorbed and may not be easily displaced by adsorbent in next adsorption cycle.
(i) Resin adsorbents (macroreticular polymer resins) generally good for removal of up to 1–2% of stream. Often regenerable.

4. *Membrane Permeation and Pervaporation* (26)
   (a) Membranes becoming more widely available for aqueous-organic separations. Some successful industrial applications reported for dehydrations of alcohols (ethanol and above), removal of alcohols from water.
   (b) Not good for services where solids, tars are expected. Stream should be distilled once before coming in contact with membrane.

3.5. Solution Evolution. It is often beneficial to reexamine a completed flow sheet and look for opportunities for simplification and consolidation of unit operations. A complicated series of unit operations can sometimes be replaced by a simpler structure that has equivalent material balance lines. When two or more sections of the flow sheet perform similar functions, ie, both produce the same product using the same or similar unit operations, one section often can be eliminated by recycling the stream to the input of the remaining section. An MSA contaminated by other components in the mixture will often function as effectively as a pure MSA, without the need for additional purification operations.

Binary System. Example: Separation of 2-Propanol–Water. Consider the separation of a binary mixture of 60 mol% water and 40 mol% IPA into two products consisting of IPA of 99.5 mol% purity and water with < 100 ppm impurity of IPA.

The first task is to examine the characteristics of the IPA–water phase equilibria (VLE, LLE, SLE) to determine the compositions of interest and any critical features. Isopropyl alcohol forms a minimum boiling azeotrope with water (80.4°C at 760 Torr, 68 mol% IPA). The azeotrope is between the feed and the IPA product and is a distillation boundary. Thus, it is impossible to obtain both desired products from any single-feed distillation column.

Table 1 contains strategic separations to be considered for crossing distillation boundaries. Many of these can be eliminated after examining the pertinent physical properties and equilibrium behavior (Table 4) and referring to the general separation heuristics in Sections 3.4.1–3.4.3. The results are summarized in Table 5.

For a binary system the two possible opportunistic distillations are essentially identical and can be combined to concentrate the feed up to $\sim$ 68% IPA and produce pure water (Table 6). The feed and products of the two possible strategic separations are still ill-defined, while those of the opportunistic separation are known.

Because a preconcentration step will probably be required to make the final sequence more economical, it is logical to start with the opportunistic separation. This separation produces one of the products, pure water, as the underflow and a concentrated distillate appropriate for feed into either strategic separation. Arbitrarily choosing pervaporation first, the retentate has a composition on the IPA-rich side of the azeotrope, while the permeate is pure water. No further strategic separations are required.

Addition of another opportunistic distillation to the flow sheet results in the production of the IPA product (bottoms) and approximately the azeotrope composition out the top. The distillate is not a desired product and must be dealt with in some fashion. It is similar in composition to several other streams in the process, so recycle (rather than further processing in additional equipment) is considered. Referring to Table 3, recycling directly back into the same column is unwise as water builds up. Recycle to the front of the process entails revaporization of this whole fraction with additional water and increases the membrane load. Recycle to the membrane inlet is probably best. Although the membrane load is increased, the fraction does not need to be distilled overhead again. The final dual-distillation, membrane permeation sequence is shown in Fig. 5. A similar sequence can be constructed using molecular sieve adsorption as the strategic separation in place of pervaporation. Both sequences involve trade-offs between water removal in the membrane or adsorption bed, recycle rate, and isopropanol production rate. Such an analysis is best carried out at the next level of detail via process simulation.

Strategies Requiring Introduction of a Third Component. Although the original binary system does not exhibit liquid–liquid behavior, Strategy (Table 5) suggests the addition of a mass separating agent to the system in order to cause the formation of a liquid–liquid region. A number of desirable characteristics for the MSA can be identified. The solvent must be partially miscible with either IPA or water, or both. Hydrocarbons, ethers, higher ketones, and halogenated compounds are usually partially miscible with water. Moreover, the liquid–liquid region must be situated to allow for crossing the azeotrope or any distillation boundaries formed. Because the MSA must be recovered at some point in the process, it should have an appreciable boiling point difference from both water and IPA. Further information on solvent selection for liquid–liquid extraction is available (34,35).

Different MSAs may lead to completely different separation systems designs. The systematic generation procedure is demonstrated for two potential solvents, hexane and methylene chloride.

Water–IPA–Hexane System. The residue curve map for the ternary system exhibits three distillation regions and a two-liquid-phase region (Fig. 6). Each pure component is the high boiling node in a different distillation region.

Thus, from the feed mixture a distillation boundary must be crossed in order to obtain pure IPA. The compositions of interest in this diagram include the feed mixture (60% water, 40% IPA), the two products (in different distillation regions), and potential MSA compositions, eg, pure hexane (high boiling node in region III), the ternary azeotrope (low boiling node in regions I, II, III), and points on the binodal curve, particularly tie-lines passing through azeotropes. Since the binary azeotropes are saddle points (and thus hard to regenerate by distillation), they are probably not good compositions to pick for an MSA. With the limited information available at this point, pure hexane is a possible MSA. This is a decision point. Another MSA composition may lead to a different flow sheet. Moreover, if may be found that pure hexane is not required.

Without revisiting the kinetic-based methods already examined for the binary case, several strategic operations can be used to cross the distillation boundary between region I and II including Mixer 1, Extractor 2, and Decanter 3. The decantation strategy could be implemented either with a single feed, which must be in the liquid–liquid region, or by adding an MSA, which puts the overall mixture in the liquid–liquid region.

The feed compositions and products of each of these strategic separations remain ill-defined. The unspecified IPA–water mixture, the input to each strategic separation, could be, but is not necessarily the original feed composition. The MSA composition (pure hexane in this case) is such that one of the products of the strategic separation is in region II (ie, the strategic separation crosses the distillation boundary). Two opportunistic distillations from the original feed mixture, Fractionators 4 and 5, are also possible. Since the feed is binary, these separations are identical and are the same as the preconcentrator previously discussed. (See Table 7).

Following step 4 of the algorithm and consulting Table 2, the first operation should be Fractionator 5, an opportunistic separation that reaches a product. None of the strategic separations is able to reach a product composition. Application of Fractionator 5 to the Feed produces the desired water product as underflow and a water–IPA mixture (D5) as distillate. Stream D5 requires further processing to obtain the IPA product. At this point no other opportunistic separations can be applied, but stream D5 is a possible input to any of the three previously identified strategic operations. Arbitrarily picking the mixing strategy, sufficient hexane must be added to D5 to produce a composition in region II.

The strategy for boundary crossing has now been implemented. However, by the addition of the hexane another critical feature has been created. Hexane must be regenerated, but it is in a different distillation region than the only remaining unprocessed stream (M1). In this case, the possible boundary crossing strategic operations are Mixer 6 and Decanter 7. Two opportunistic distillations, Fractionators 8 and 9, can also be applied to M1 (note decantation is also a possible opportunistic separation).

Again referring to Table 2, the next separation should be Fractionator 9, which produces the IPA product directly. If the distillation is driven far enough stream D9 will be in the two-phase region and will be an appropriate input into the strategic separation Decant 7. Decanter 7 yields phases in regions I and III. Alternatively, D9 could be mixed with a sufficient amount of some stream (unknown at this time) in region III to bring the overall mixture into region

III. Either strategy could be selected, but the decant is probably better as it can be accomplished without the addition of another stream. The organic phase of the decanter, O7, is in region III and needs to be further purified to obtain pure hexane. Two opportunistic separations, Fractionators 10 and 11, are possible.

Selection of Fractionator 11 gives pure hexane, which can be recycled to Mixer 1. The distillate D11, however, is a problem. It cannot be distilled because of its location next to a distillation boundary. It is outside of the two phase region, so it cannot be decanted. In essence, no further separations are possible. However, using the rules of Table 3, it can be mixed into the MSA recycle stream without changing the operation of Mixer 1 appreciably. However, as both outlet streams are mixed together, Fractionator 11 is not really needed. The mixture of hexane and IPA, O7, could have been used as the MSA composition in the first place.

The final loose end in the process is the aqueous decanter product, A7. The hexane must be removed before the mixture can be sent to waste water treatment (ie, accepted as a water by-product). Two opportunistic separations, Fractionators 12 and 13, are possible. Selection of Fractionator 13 gives pure water underflow, and a distillate similar to D5. Distillate D13 can be recycled back and mixed with D5 without affecting the operation of Mixer 1. All streams have now been processed and the flowsheet produces both desired products (Fig. 6**b**).

Although the flowsheet is complete, it does contain some redundant separation that adds to the capital cost. With the basic structure defined, the next step is to consider some evolutionary improvements. First, Fractionator 13 performs essentially the same job as Fractionator 5, ie, concentrating a mixture of water and IPA. Fractionator 13 can be taken out and A7 can be recycled directly to the feed of Fractionator 5. Although the flowrate to Fractionator 5 increases, its basic separation function does not change. As the bubble point of A7 is somewhat higher than that of Feed F, A7 is probably best introduced as a separate feed lower in the column. Second, using pure hexane as the MSA was unnecessary. Fractionator 11 can be eliminated and O7 used as the MSA composition. Finally, considering the bubble point and amount of O7, operations Mixer 1, Fractionator 9, and Decanter 7 can be rearranged as a distillation-decanter combination with identical overall material balance lines and function. The evolved flowsheet is shown in Fig. 6**c** and **d**. Other sequences can be generated by choosing different alternatives at the various decision points.

Methylene Chloride Alternatives. When the solvent is changed to methylene chloride the residue curve map contains two distillation regions and a liquid–liquid region (Fig. 4**b**). Pure methylene chloride is a saddle in distillation region II and therefore is probably not a good choice for the MSA composition. Rather, the compositions of interest are the water–methylene chloride azeotrope (high boiling node), points on the binodal curve, and IPA-free mixtures of methylene chloride and water with compositions between those of the binodal curve and the methylene chloride–water azeotrope. The strategic operations are the same as with the hexane case (decant, extract, or mix) and again, two opportunistic fractionations are possible (preconcentration distillations).

In one possible sequence, the MSA composition is chosen as water saturated methylene chloride expected to be regenerated by decantation. The boundary-crossing strategic operation is to mix the feed with the MSA. The resulting two-phase mixture is opportunistically fractionated to produce the IPA product as bottoms, a mixture of water–methylene chloride as distillate. This distillate is opportunisticly decanted to recover water-saturated methylene chloride MSA for recycle. The aqueous decanter phase is the water product, which optionally may be further purified by stripping (Fig. 7).

If an opportunistic preconcentration of the feed is used instead, an entirely different flowsheet results. In this case the MSA composition is a two-phase mixture of methylene chloride and water. Detailed simulations are required to determine which of these (or other) IPA dehydration flowsheet alternatives is the economically advantaged process.

4. Flowsheet Generation for Reactive Systems

4.1. Problem Representation. The integration of chemical reaction with separation offers the potential of significant capital and operating cost reductions. Consequently, many different types of reactive separations have been propounded including reactive distillation, extraction, absorption, crystallization, and adsorption (36,37). As with nonreactive systems, effective graphical techniques have been developed to help visualize the superposition of complex chemical and phase equilibrium. When the number of components of a reactive system is > 3, it becomes more difficult to visualize composition-based phase diagrams, as tetrahedral or higher order constructs are required. However, by the Gibb's phase rule, the number of degrees of freedom of a system in simultaneous phase and chemical equilibrium is reduced by the number of independent equilibrium reactions. Thus, the reactive phase diagram is constrained to lie on a subset of surfaces embedded in the overall composition space. These surfaces can be transformed into lower dimensional composition coordinates, often referred to as *transformed* or *reaction invariant* composition space (4). The transformed compositions, although dependent on the number and type of reaction, are independent of the extent of reaction. For a system of n components with r reactions, the transformed liquid mole fraction, X_i, is given by

$$X_i = \left(\frac{x_i - v_i^T (v_{\text{ref}})^{-1} x_{\text{ref}}}{1 - v_{\text{tot}}^T (v_{\text{ref}})^{-1} x_{\text{ref}}} \right) \qquad \text{for } i = 1 \text{ to } n - r$$

where $v_i^T =$ row vector of stoichiometric coefficients of component i for each reaction r
$v_{\text{ref}} =$ square matrix of stoichiometric coefficients of r reference components for each reaction r
$x_{\text{ref}} =$ column vector of mole fractions of reference components
$v_{\text{tot}}^T =$ row vector of the sum of stoichiometric coefficients for each of r reactions

A similar equation can be defined for the transformed vapor fractions, Y_i. The reference components are a subset of the reacting species and are used to indicate the extents of reaction in terms of the mole numbers of the reference components. The number of reference components is equal to the number of independent reactions. Selection of the proper reference component is system dependent. Selection rules have been elucidated (38) and the transformed coordinate approach has been applied to a variety of reactive separations and phase equilibria including reactive distillation, adsorption, and solid–liquid, liquid–liquid equilibria (39–41).

Transformed compositions are particularly useful for visualization of reactive distillation systems. It has become well established that phase and distillation region diagrams (DRD) in transformed compositions are entirely analogous to those for nonreactive systems, exhibiting the same material balance properties. Thus, reactive DRD can be used to assist in design feasibility and operability studies in much the same fashion as outlined above for non-reactive, nonideal systems (3,4,42).

When an equilibrium reaction occurs in a vapor–liquid equilibrium system, the phase compositions depend not only on the relative volatilities, but also on the consumption or production of species. The condition for azeotrope formation (vapor and liquid-phase compositions are equal for two or more components) no longer holds true in a reactive system and must be modified to include reaction stoichiometry:

$$\frac{y_1 - x_1}{v_1 - v_T x_1} = \frac{y_i - x_i}{v_i - v_T x_i} \qquad \text{for all } i = 2 \text{ to } n - 1 \quad \text{and} \quad v_T = \sum_{i=1}^{n} v_i$$

where x_i, y_i = mole fractions in the liquid and vapor, respectively, and v_i = stoichiometric reaction coefficient (negative for reactants, positive for products).

A *reactive azeotrope* occurs at a temperature where the rate of mass exchange between phases and the rate of reaction for each component are such that no net change in composition occurs in either phase. Whether one assumes equilibrium reaction behavior or kinetically controlled reaction behavior (very much dependent on column holdup, catalysis, and other device implementation parameters) affects the existence and location of reactive azeotropes. Reactive azeotropes always lie on the chemical equilibrium line. Since the boiling points of the mixture are affected by the column pressure, and the equilibrium constant is influenced by temperature (and thus column pressure), the location of the reactive azeotrope can be influenced by changing the column pressure.

A residue curve map in transformed coordinates for the reactive system methanol–water–acetic acid–methyl acetate is shown in Fig. 8. The water–methyl acetate azeotrope has disappeared (water and methyl acetate can back react to methanol and acetic acid), while the methyl acetate–methanol azeotrope remains. Only those azeotropes containing either all the required reactants or products will be altered by the reaction. The system exhibits only one distillation region in which the methanol–methyl acetate azeotrope is the low boiling node and acetic acid is the high boiling node.

4.2. Flow Sheet Construction.

Because of the analogous properties of reactive and nonreactive residue curve maps, the opportunistic-strategic synthesis methods described earlier can be extended to reactive system synthesis.

There has been limited progress in this direction (44,45). The elucidation of an elegant reactive separation solution to a complex synthesis problem is often an appealing prospect. However, there must be good reasons for combining reaction and separation. Reactive separations introduce added design and operability difficulties that must be weighed against any perceived benefits. In practice, the operability space of a reactive separation is often quite limited compared to sequential reaction and separation. For example, reactive distillation is only applicable when the mixture boils under temperature and pressure conditions favorable for the reaction. Other minimum compatibility criteria must also be met. Other unfavorable situations for reactive distillation are the presence of appreciable solids, operation at supercritical conditions, ie, where no separate vapor and liquid phases exist, operation at very high or low temperature and pressure conditions, ie, vapor and liquid phases both must be present and appropriate heating and cooling media available.

Once the minimum compatibility criteria have been met, then it is necessary to evaluate whether simultaneous separation of components from the reaction mixture is beneficial. Typical favorable situations include (*1*) when the reaction must be carried out with a large excess of one or more of the reactants; (*2*) when a reaction can be driven to completion by removal of one of the products as formed, ie, equilibrium limited reactions; (*3*) when the desired product is formed as an intermediate of consecutive reaction steps and can be removed as formed (improvement of selectivity); (*4*) when a parallel reaction pathway can be shutdown by manipulating local concentration gradients; (*5*) when exothermic heat of reaction can be used to boil the mixture; (*6*) when narrow temperature control is required and the mixture can be made to boil at the appropriate reactions conditions.

A parametric study has been completed on component relative volatilities and magnitude of reaction equilibrium constants for the generic equilibrium reaction systems: $A \leftrightarrow C$, $A \leftrightarrow C + D$, $A + B \leftrightarrow C$, $A + B \leftrightarrow C + D$ (46). In this work the liquid-phase behavior was assumed to be ideal. Reactive azeotropes could exist, but no nonreactive azeotropes were allowed. The following observations about the four types of reaction systems with ideal liquid-phase behavior were made: (*1*) every $A \leftrightarrow C$ system has one and only one reactive azeotrope, independent of relative volatilities, but dependent on the magnitude of the reaction equilibrium constant, K_{eq}; (*2*) for the $A \leftrightarrow C + D$ system, reactive azeotropes are only present for $K_{\text{eq}} < 1$, and if present do no limit the economic viability; (*3*) for the $A + B \leftrightarrow C$ system, reactive azeotropes can affect economic viability when both reactants are lower or higher boiling than the product; (*4*) for the $A + B \leftrightarrow C + D$ system, all reactive azeotropes are intermediate boiling and if present, can affect economic viability when either C and D are higher boiling than A and B and relative volatilities follow $\alpha_{AB} > 1$, $\alpha_{AD} > \alpha_{AC}$, $\alpha_{AB} < \alpha_{AD}$, or C and D are lower boiling than A and B and relative volatilities follow $\alpha_{AB} > 1$, $\alpha_{AC} < 1$, $\alpha_{AD} < 1$, $\alpha_{AC} > \alpha_{AD}$.

A number of configuration and economic viability heuristics derived from this work are summarized in Table 8. These heuristics also serve as a starting point for consideration of reactive systems with nonideal liquid-phase behavior. Subawalla and Fair also presented some basic reactive distillation heuristics

(47). A number of examples of reactive distillation synthesis using various synthesis methods have been published (3,4,48–50).

Example: Methyl Acetate Production. Consider the process for the production of methyl acetate via the acid-catalyzed equilibrium-limited esterification of methyl with acetic acid, with by-production of water. The reaction is nearly athermic, with an equilibrium constant on the order of unity.

Conventional Flowsheet. Assuming that a conventional reactor (eg, CSTR) Using the synthesis approach outlined above, it is possible to develop a The effluent from the reactor comprises the esterification products of methyl acetate and water, as well as unreacted methanol and acetic acid. The four component system exhibits azeotropic behavior, with binary low boiling azeotropes between and methyl acetate–water, and methanol–methyl acetate (homogenous and lowest boiling point of mixture). The methyl acetate–water azeotrope is heterogeneous, but the azeotropic composition is outside of the liquid–liquid region. There are no other binary or ternary azeotropes, although the acetic acid–water system exhibits a tangent pinch at the water-rich end.

The first opportunistic separation takes all of the methyl acetate, and methanol overhead with as much water as azeotropes with the methyl acetate. The overhead of the first column comprises a ternary system in which both methyl acetate and methanol are saddles. Examining the residue curve map for this system, the strategic separation of extractive distillation can be used to draw methanol down the column and reject methyl acetate out the top. Solvents, eg, ethylene glycol, water, and acetic acid, are potential extractive distillation solvents. This methyl acetate may be wet with water, so if desired an additional opportunistic separation can be used to take the methyl acetate–water azeotrope overhead (recycled to the extractive distillation column) and pure methyl acetate out the bottom. Methanol for recycle is recovered by distilling the underflow of the extractive distillation column.

The bottoms from the effluent splitter column containing the acetic acid can be recovered by using a combination of strategic separation separations for pinched systems. Adding an extraction agent, eg, ethyl acetate, to concentrate the acetic acid, followed by heterogeneous azeotropic distillation to recover the acetic acid and solvent finishes the flow sheet (Fig. 9).

Evolution to Reactive Distillation. The conventional flowsheet thus far synthesized could be summarized as consisting of a number of sections or tasks as in Fig. 10. It turns out that the economically expensive task in the process is the separation of acetic acid from coproduct water. However, if reactive distillation were exploited, acetic acid might be reacted to completion thereby eliminating the acid–water separation requirement. For this system for which K_{eq} is on the order of 1, the order and magnitude of the relative volatilities and the heuristics in Table 8 suggest that reactive distillation might be economically advantageous. The residue curve map in transformed coordinates for this system shown in Fig. 8 shows no distillation boundaries. However, as noted previously, the methyl acetate–methanol azeotrope remains, and both desired products from the process, methyl acetate and water, are saddles that cannot be reached in high purity and recovery by reactive distillation alone.

The process tasks might be developed as follows. The reaction task is followed by reactive distillation to react all acetic acid remaining in the water from the reactor effluent. The water stream may contain methyl acetate and methanol, which may be opportunistically removed by distillation, taking some water as the methyl acetate–water azeotrope, and recycled. Reactive distillation can also be employed to react all methanol remaining in the methyl acetate from the reactor effluent. The methyl acetate stream still contains water as an azeotrope, and this azeotrope may be broken by extractive distillation with acetic acid and any remaining acetic acid also removed by opportunistic distillation from the methyl acetate product and recycled. The resulting process tasks and recycles are arranged as in Fig. 11.

Six of the seven tasks in the process of Fig. 11 are distillative in nature and each can be implemented in its own piece of equipment with optimized column design parameters, hydraulics, reflux ratio, etc. For this particular example, considering the fortuitous placement of recycles from each task, it is possible to integrate all seven tasks and their energy requirements into a single column shell with a single reboiler and condenser as in Fig. 12. The resulting distillation–reactive distillation–extractive distillation column requires ~ 80% less capital and energy that the conventional flow sheet in Fig. 9.

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Table 1. **Strategic Separations**

Strategy	Separation implementation	Comments
	Pinched Regions	
use existing liquid–liquid region or add component that causes new or altered liquid–liquid region	decanter liquid–liquid extraction	By-passes pinched VLE
exploit solid–liquid equilibrium to circumvent–cross-pinch	melt crystallization adsorption	driving force for melt cryst. is a melting point difference of impurities and desired product. Feed must meet certain melting point and crystal characteristics for feasibility (see also solution crystallization)
change system pressure to alter–eliminate pinch	distillation	feasibility highly dependent on extent that pinch is altered by moderate change in pressure
exploit solid–liquid solubility differences	solution crystallization	based on differences in melting points and liquid-phase solubilities. Four modes of operation possible: drown out, isothermal evaporation, adiabatic evaporation, cooling. Choice depends on stream characteristics
exploit kinetic phenomena to circumvent–cross-pinch	molecular sieve adsorption membrane permeation pervaporation	requires the selection of solid-phase mass separation agent
use VLE to circumvent–cross-pinch. Approach pinched region from nonpinched direction	distillation azeotropic distillation	choose third component which does not form pinch with one of the key components
distill through pinched region	simple distillation	process may require a large number of stages and a high reflux ratio
use existing component or add new MSA to by-pass pinch in a two-feed column	extractive distillation	extractive agent modifies liquid-phase behavior (activity coefficients) of key components. Residue curve map must be of appropriate form for extractive distillation to work
	Saddle Products	
use existing liquid–liquid region or add component that causes new or altered liquid–liquid region	decanter liquid–liquid extraction	a binodal composition is often not pure enough for the final product. It may still be difficult to perform the additional purification

Table 1. (*Continued*)

Strategy	Separation implementation	Comments
exploit solid–liquid equilibrium to reach saddle	melt crystallization adsorption	driving force for melt cryst. is a melting point difference of impurities and desired product. Feed must meet certain melting point and crystal characteristics for feasibility (see also solution crystallization)
use existing component or add new MSA to reach saddle in a single two-feed column	extractive distillation	extractive agent modifies liquid-phase behavior (activity coefficients) of key components. Residue curve maps must be of appropriate form for extractive distillation to work
exploit solid–liquid solubility differences to reach saddle	solution crystallization	based on differences in melting points and liquid phase solubilities. Four modes of operation possible: drown out, isothermal evaporation, adiabatic evaporation, cooling. Choice depends on stream characteristics
reduce or expand the dimensionality of problem to turn saddle into a node; move to a face of the RCM	azeotropic distillation distillation	a saddle in a three-component system becomes a node in a two-component system. Adding the appropriate component can alter the dist. region boundaries and turn a saddle into a node
exploit kinetic phenomena to reach saddle	adsorption membrane permeation pervaporation	requires the selection of solid-phase agent
react to turn saddle into node	reaction reactive distillation	reactions involve components already in mixture
	Overcoming Distillation Boundaries	
use existing liquid–liquid region or add component that causes new or altered liquid–liquid region	decanter liquid–liquid extraction	uses LLE to avoid boundary in VLE
exploit solid–liquid equilibrium	melt crystallization adsorption	driving force for melt cryst. is a melting point difference of impurities and desired product. Feed must meet certain melting point and crystal characteristics for feasibility (see also solution crystallization)

Table 1. (*Continued*)

Strategy	Separation implementation	Comments
mix streams to cross-boundary	mixer	may generate infeasible solutions due to mass balance violations. Only works if there is a way to get a composition that is purer than the desired mixture product (farther than the middle point of the balance)
exploit existing convex curvature or add component that causes favorable convex curvature to cross boundary	distillation	curvature is difficult to predict accurately without experimental data. Boundary must be highly curved to avoid large recycles
change system pressure to alter–eliminate boundary	distillation	feasibility highly dependent on extent that azeotrope composition is altered by moderate change in pressure
exploit solid–liquid solubility differences	solution crystallization	based on differences in melting points and liquid phase solubilities. Four modes of operation possible: drown out, isothermal evaporation, adiabatic evaporation, cooling. Choice depends on stream characteristics
exploit kinetic phenomena to cross-boundary	molecular sieve adsorption membrane permeation pervaporation	requires the selection of solid-phase agent
	Vapor–Solid–Liquid Equilibria	
use intermediate reflux of low melting point component to prevent freezing of high melter	sidedraw-reflux column	occurs when boiling and melting points of components overlap
exploit solid–liquid equilibrium to separate overlapping melters–boilers	melt crystallization	driving force for melt cryst. is a melting point difference of impurities and desired product. Feed must meet certain melting point and crystal characteristics for feasibility (see also solution crystallization)
add a component to strip out lighter components to separate overlapping melters–boilers	stripping	

Table 1. (*Continued*)

Strategy	Separation implementation	Comments
exploit solid–liquid solubility differences to separate overlapping melters–boilers	solution crystallization	based on differences in melting points and liquid phase solubilities. Four modes of operation possible: drown out, isothermal evaporation, adiabatic evaporation, cooling. Choice depends on stream characteristics
	Temperature Sensitive Mixtures	
use existing liquid–liquid region or add component that causes new or altered liquid–liquid region	decanter liquid–liquid extraction	perform separation at conditions below reaction–degradation temperature: usually can be accomplished at temperatures between 20 and 45°C
exploit solid–liquid equilibrium	melt crystallization adsorption	driving force for melt cryst. is a melting point difference of impurities and desired product. Feed must meet certain melting point and crystal characteristics for feasibility (see also solution crystallization)
alter system pressure to decrease reboiler temperature	vacuum distillation wiped film evaporation short-path evaporation	feasibility highly dependent on pressure required to prevent degradation and stage requirements of desired separation
exploit solid–liquid solubility differences	solution crystallization	based on differences in melting points and liquid phase solubilities. Four modes of operation possible: drown out, isothermal evaporation, adiabatic evaporation, cooling. Choice depends on stream characteristics
exploit kinetic phenomena	molecular sieve adsorption membrane permeation	requires the selection of solid-phase agent

Table 2. **Rules for Selecting Among Potential Operations**

Tier 1	Once all the potential opportunistic and strategic operations have been identified for the current stream, then the next step is to determined the order that these operations should be tried. Use the following heuristics to order alternatives at a decision point: 1. Select a strategic separation that reaches a product (or MSA) composition. 2. Select an opportunistic separation that reaches a product (or MSA) composition. 3. Select a strategic operation that does not reach a product. 4. Select an opportunistic operation that reaches the feed composition of a strategic operation. 5. Select any remaining opportunistic separation.
Tier 2	When more than one separation is feasible: 1. Perform hardest separations last. 2. Favor separations that remove corrosive, hazardous components as a product directly (ie, no further separation required for that stream). 3. Favor separations that remove the largest fraction of mixture as a product directly. 4. Favor separations that give approximately equal-sized output streams.

Table 3. **Recycle Heuristics**

1. Consider recycling a stream when the separation(s) to be performed on that stream would duplicate a section of the process that has been previously specified. This will generally occur when the composition of a stream is very similar to the composition of a previous stream in the process.
2. Avoid recycle to a point that would allow infinite build-up of any component, ie, if there is no outlet for each component downstream of a recycle, then do not recycle to that point.
3. Similarly to item No. 2, if a stream is the last stream on the source list, and all products have not been obtained, recycle is not an option.
4. Match stream compositions as much as possible.
5. Avoid recycle of streams that cause major changes in the operation of upstream units, eg, do not recycle a stream at a point that would cause an upstream composition to move into another distillation region.
6. If compositions do not match, and item No. 5 is not violated, then it is permissible to recycle a stream that is small compared to an upstream flow rate.
7. If all product specs have been met and all critical features dealt with, and there are still streams on the source list, then consider recycling remaining streams.
8. Do not add a new MSA if all products and MSA compositions of interest have been reached and there are still streams on the source list: consider recycling remaining streams.

Table 4. **Characteristic Properties for Liquid Separation Methods**

Separation method	Properties
Distillation-Based Methods	
distillation	relative volatility D/B ratio of mixture residue curve map or distillation region diagram
extractive distillation	data, model for liquid-phase behavior residue curve map or distillation region diagram
azeotropic distillation	residue curve map or distillation region diagram
pressure-swing distillation	effect of pressure on azeotrope composition type of azeotrope (max or min boiling)
distillation into curved boundaries	detailed, accurate residue curve map
high vacuum distillation	effect of pressure on boiling points relative volatility
Crystallization Methods	
adiabatic evaporation	effect of temperature on solubility boiling point of solvent heat of vaporization of solvent
isothermal evaporation	effect of temperature on solubility boiling point of solvent heat of vaporization of solvent
cooling	effect of temperature on solubility eutectic diagram
drown-out or salt-out	solubility in solvent
melt crystallization	melting points eutectic diagram metastable zone width
Other MSA Methods	
steam stripping	miscibility with water azeotrope formation with water reactivity with water
extraction	data, model for liquid-phase behavior selectivity in solvent
adsorption	kinetic diameter hydrogen bonding characteristics
pervaporation	chemical families

Table 5. **Strategic Separations for Crossing Distillation Boundaries: IPA–Water**

Strategy	Heuristic	Status	Comments
use existing liquid–liquid region or add component that causes new or altered liquid–liquid region	III.2.(c)	extraction, decantation infeasible with current system	water and 2-propanol miscible in all proportions no liquid–liquid region in binary system
	III.2.(a)	may be feasible with addition of suitable MSA	components show different liquid phase behavior. Exploitation of LLE possible with appropriate MSA
exploit solid–liquid equilibrium	II.6.(i)	melt crystallization probably inferior	possibly feasible, but freezing points of water and 2-propanol (273 and 184.7 K, respectively) relatively low
	III.3.(c)	adsorption infeasible	strongly hydrogen-bonded, miscible system. Adsorption probably unfavorable
mix streams to cross-boundary		mixing infeasible	binary azeotropes cannot be broken in practice by simple mixing. Would either require infinite recycle or mixing of IPA that is purer than the desired product
exploit existing curvature or add component that causes favorable curvature to cross boundary	I.5.(d)	infeasible alternative	no convex curvature to exploit since azeotrope is point in phase diagram
		may be feasible with addition of suitable third component	
change system pressure to alter–eliminate boundary	I.4.(a)	pressure-swing distillation infeasible	azeotropic composition varies only slightly with pressure: 13 vol% water at 95 Torr; 12 vol% water at 760 Torr, 11.7 vol% water at 3087 Torr
exploit solid–liquid solubility differences	II.1.(a)	solution crystallization probably inferior	low temperatures required (well < 0°C)

Table 5. (*Continued*)

Strategy	Heuristic	Status	Comments
exploit kinetic phenomena to cross-boundary	III.3.(a)	molecular sieve adsorption feasible with preconcentration	difference in kinetic diameters (water 2.65 Å; IPA 4.2 Å) acceptable for 3-A mol sieves. Large amount of water to adsorb; preconcentration step probably necessary to keep bed size reasonable
	III.4.(a)	membrane permeation feasible with preconcentration	dehydration of IPA known application of pervaporation (eg, cellulose acetate membranes). Large amount of water to pass through membrane, preconcentration step probably necessary to keep membrane area reasonable

Table 6. **Opportunistic Distillations, Binary System**

Operation	Unit OPS	Feed(s)	Products
opportunistic separations from feed	fractionator	feed mixture: 40% IPA	D - IPA/water azeotrope B - water (target product)
strategic operations from feed	molecular sieve adsorption	undefined IPA/ water mix	adsorbed - water raffinate - mixture enriched in IPA
	membrane permeation		permeate - water raffinate - mix enriched in IPA

Table 7. **Strategic Separations for Crossing Distillation Boundaries: Water–IPA–Hexane**

Operation	Unit OPS	Feed(s)	Products
strategic operations for reaching region II	mixer 1	undefined IPA/water mix MSA	M1 - mixture in region II
	extractor 2	undefined IPA/water mix MSA	E2 - extract in region II R2 - raffinate in region I
	decanter 3	undefined IPA/water/MSA mix	O3 - organic phase in region II A3 - aqueous phase in region I
opportunistic separations from feed	fractionator 4	feed mixture: 40% IPA	D4 - IPA/water azeotrope B4 - ≈water
	fractionator 5	feed mixture: 40% IPA	D5 - IPA + water B5 - water (target product)
strategic operations for reaching region III	mixer 6	undefined mixture in region II	M6 - mixture in region III
	decanter 7	undefined mixture in region II	O7 - organic phase in region III A7 - aqueous phase in region I
opportunistic separations from mixture M1	fractionator 8	M1	D8 - ternary azeotrope B8 - IPA + hexane, or IPA + water
	fractionator 9	M1	D9 - hexane + IPA + water B9 - IPA (target product)
opportunistic separations from decant phase O7	fractionator 10	O7	D10 - ternary azeotrope B10 - hexane + IPA
	fractionator 11	O7	D11 - hexane/IPA azeo + water B11 - hexane (target MSA)
opportunistic separations from decant phase A7	fractionator 12	A7	D12 - ternary azeotrope B12 - water + IPA
	fractionator 13	A7	D13 - IPA/water azeo + hexane B13 - water (target product)

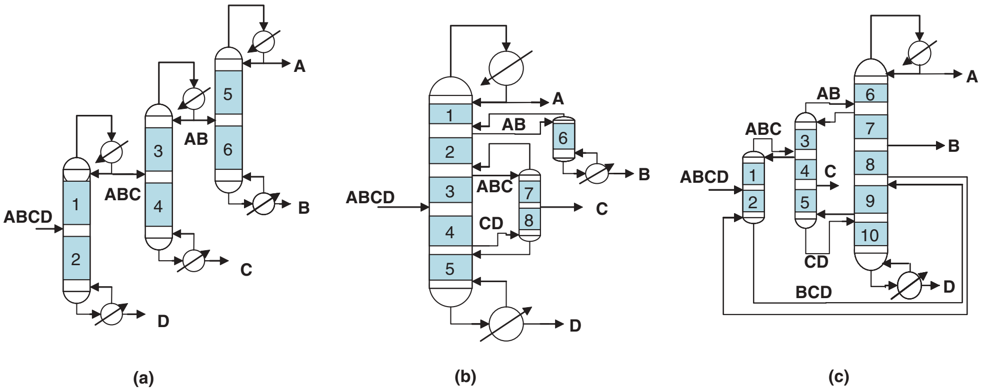
Table 8. **Reactive Distillation Heuristics**

Configuration Heuristics

1. Systems with low boiling reactive azeotropes and low boiling products must have a nonreactive rectifying section to produce a pure product
2. Systems with high boiling reactive azeotropes and high boiling products must have a nonreactive stripping section to produce a pure product
3. A double feed column is usually best when the reactant boiling points are far apart ($\alpha_{AB} \geq 4$)
4. A single feed column is usually best when the reactant boiling points are close ($1.2 \geq \alpha_{AB} \geq 1$)
5. A column comprising a center reactive zone, nonreactive stripping and rectifying sections is generally favorable for $A \leftrightarrow C + D$ and $A + B \leftrightarrow C + D$ systems
6. The ability to separate C from D dictates the economic viability of reactive distillation for $A \leftrightarrow C + D$ and $A + B \leftrightarrow C + D$ systems, assuming $K_{eq} > 1$. For a reactive distillation to be economically viable and:

   (a) To have reflux ratio ≤ 100, then should have $\alpha_{CD} > 1.1$
   (b) To have reflux ratio ≤ 10, then should have $\alpha_{CD} > 1.25$
   (c) To have reflux ratio ≤ 5, then should have $\alpha_{CD} > 1.45$
   (d) To have reflux ratio ≤ 2.5, then should have $\alpha_{CD} > 2.1$

7. For systems in which the reactants are all intermediate boiling and the products are the highest and lowest boiling components, then a K_{eq} of at least 10^{-5} is required for potential economic viability
8. For systems in which the products are all intermediate boiling and the reactants are the highest and lowest boiling components, then a K_{eq} of at least 100 is required for potential economic viability
9. For systems in which the desired product is the highest boiling component, then a K_{eq} of at least 0.1 is required for potential economic viability
10. For systems in which the desired product is the lowest boiling component, then a K_{eq} of at least 10^{-3} is required for potential economic viability
11. For systems in which the by-product is the lowest boiling component and the desired product is intermediate boiling, then a K_{eq} of at least 10^{-3} is required for potential economic viability
12. For systems in which the by-product is the highest boiling component and the desired product is intermediate boiling, then a K_{eq} of at least 10^{-2} is required for potential economic viability



(a) (b) (c)

Fig. 1. Four Component Separation Sequence: (**a**) noncoupled direct sequence, (**b**) thermally coupled with 8 sections and 3 reboilers and condensers, and (**c**) thermally coupled with 10 sections and 2 reboilers and condensers.

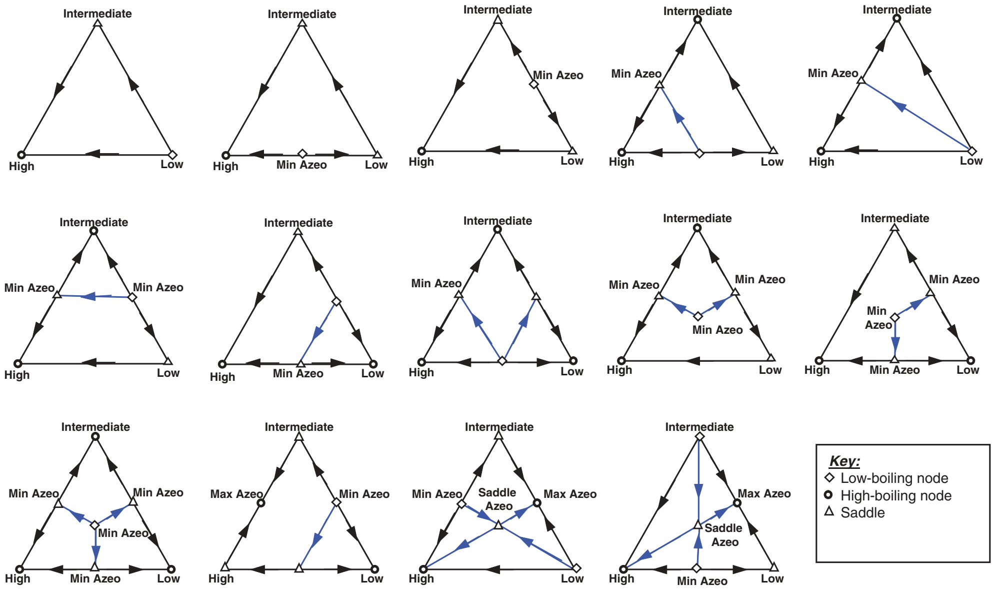
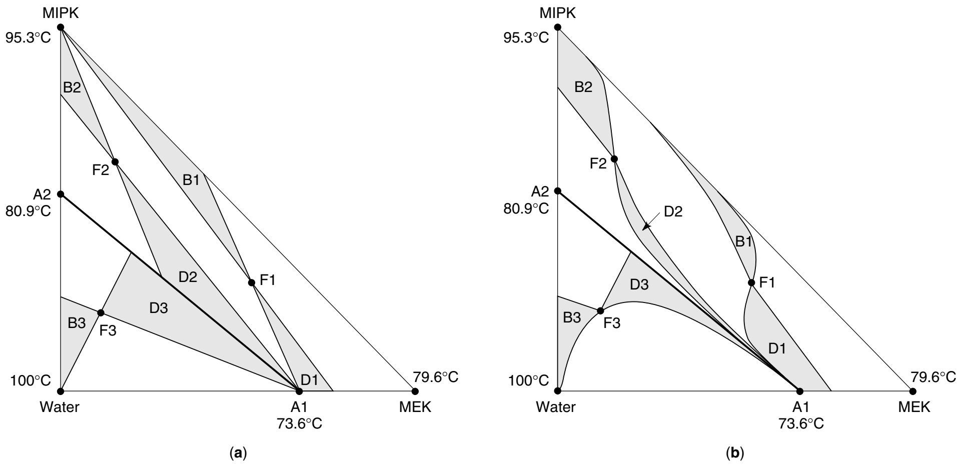


Fig. 2. Fourteen most common DRD.



(**a**) (**b**)

Fig. 3. Methyl ethyl ketone–MIPK–water system, where A1 and A2 represent two different azeotropes; F1, F2, and F3, different feed compositions; B*n* and D*n* the corresponding bottoms and distillates, respectively; (—), the distillation boundary; and (Ξ), the reachable compositions for the various feeds: (**a**) approximate bow-tie and (**b**) exact reachable compositions.

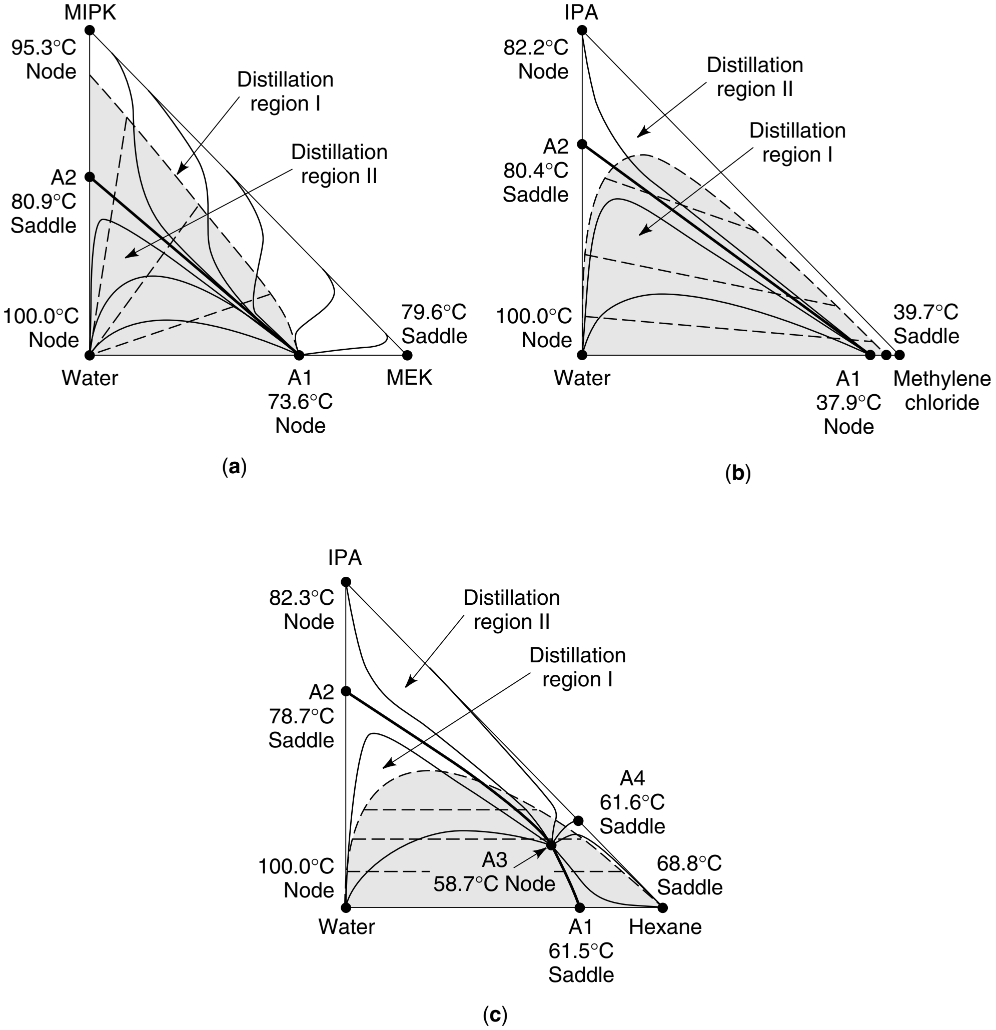


Fig. 4. Combined residue curve and phase equilibria diagrams for the systems where A1-4 represent azeotropes, (—) is the distillation boundary, the shaded areas represent the region of two liquid phases, and (– – –) are tie lines: (**a**) MEK–MIPK–water; (**b**) methylene chloride–IPA–water; and (**c**) hexane–IPA–water.

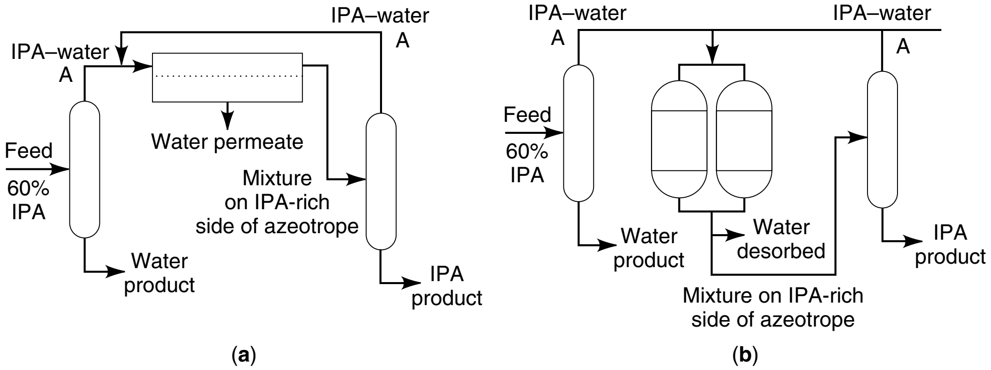


Fig. 5. Distillation of aqueous 2-propanol (IPA), where A is the azeotrope, combined with (**a**) pervaporation and (**b**) adsorption.

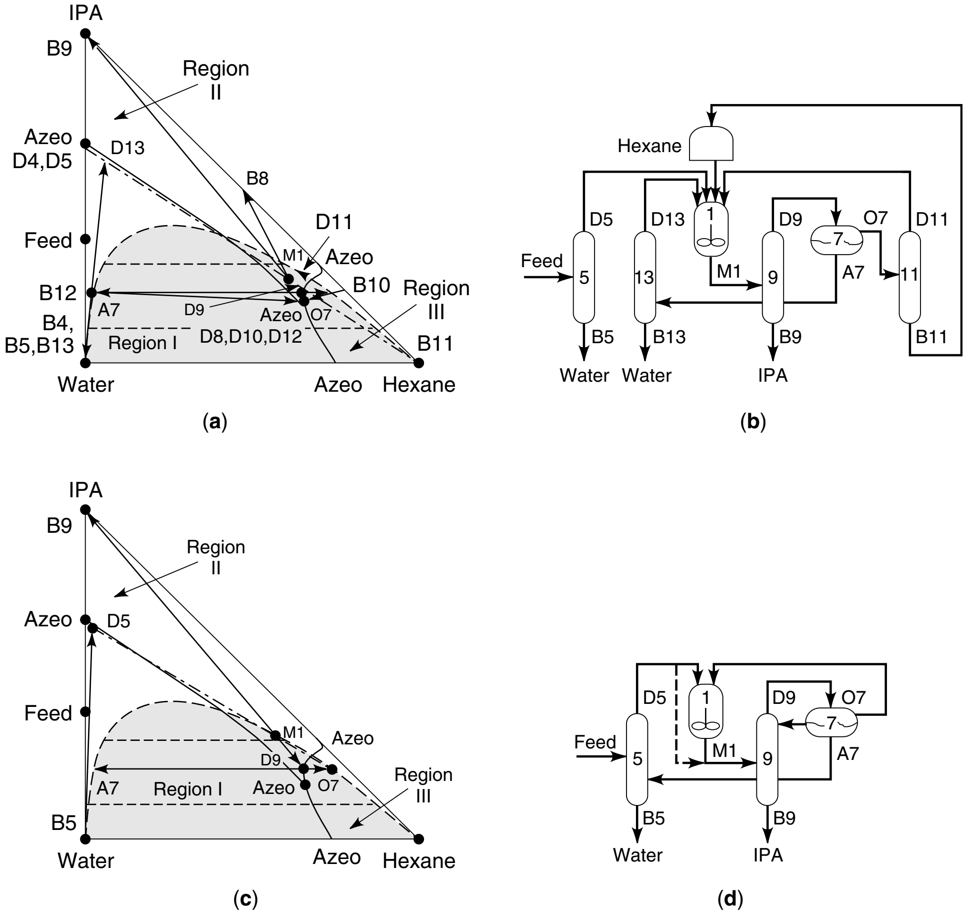
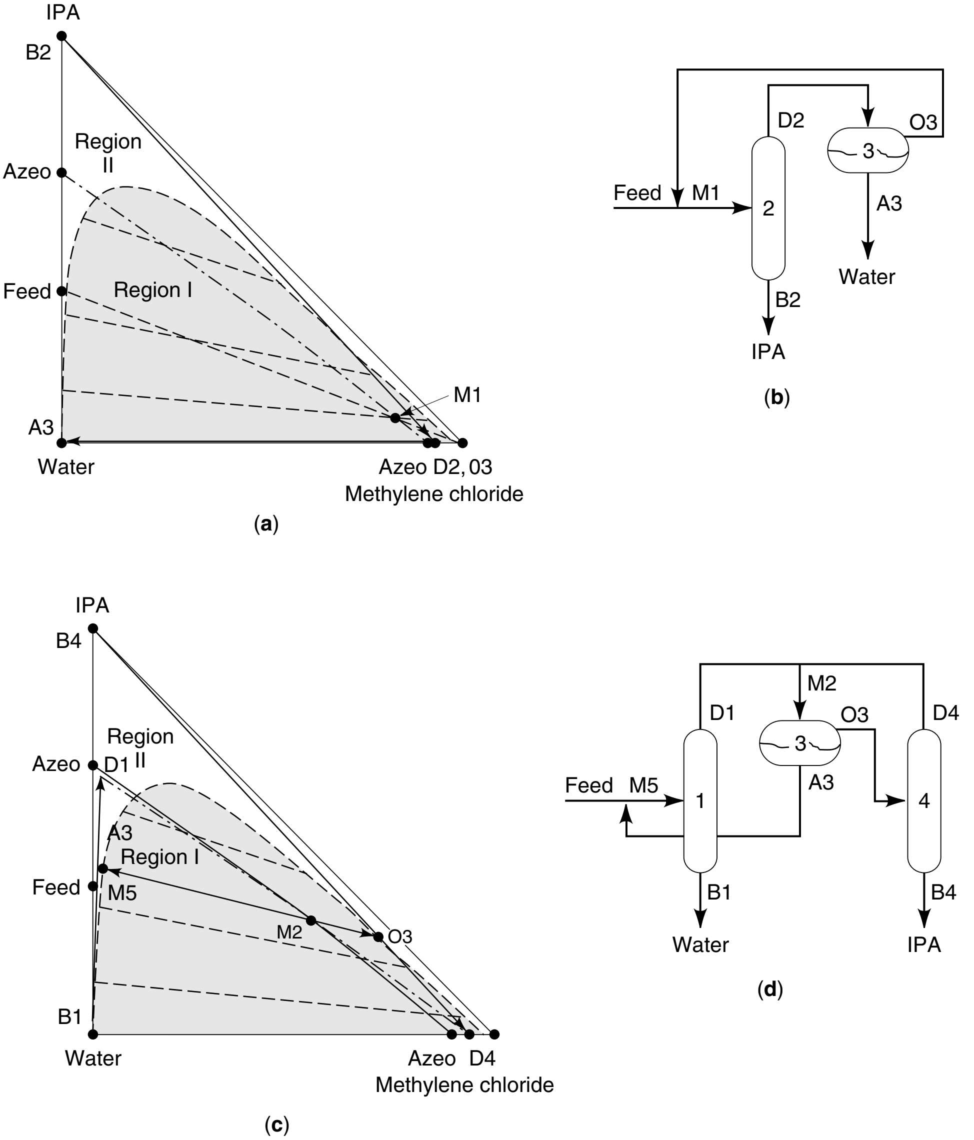


Fig. 6. Isopropyl alcohol dehydration where Azeo is azeotrope, (– – –) are tie lines, and the shaded areas represent the region of two liquid phases. Initial dehydration (**a**) residue curve map and (**b**) flow sheet, and evolved IPA dehydration (**c**) residue curve map and (**d**) flow sheet. The ~ in **b** and **d** represent a two-phase decanter. (See text; see Table 7.)



(**a**)

(**b**)

(**c**)

(**d**)

Fig. 7. Isopropyl alcohol dehydration using methylene chloride where Azeo = azeotrope, the shaded areas represent the region of two liquid phases, (– – –) are tie lines, and ~, two-phase decanters: (**a**) residue curve map and (**b**) flow sheet, and alternative methylene chloride (**c**) residue curve map and (**d**) flow sheet. (See text.)

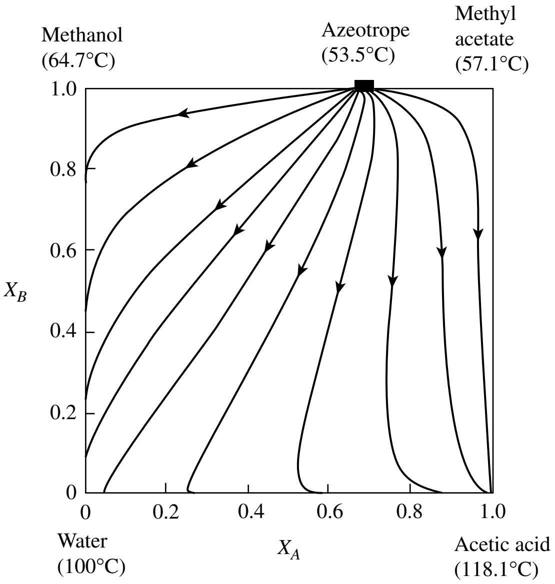


Fig. 8. Reactive residue curve map for a methyl acetate system. (Reprinted from Ref. 43, with permission from Elsevier.)

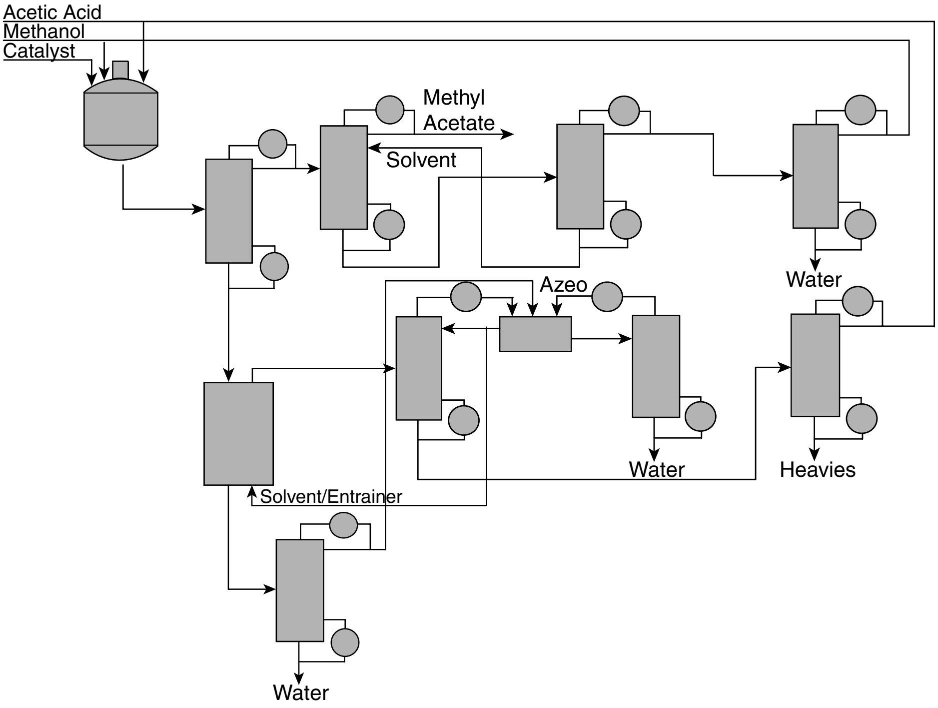


Fig. 9. Conventional flowsheet for methyl acetate process.

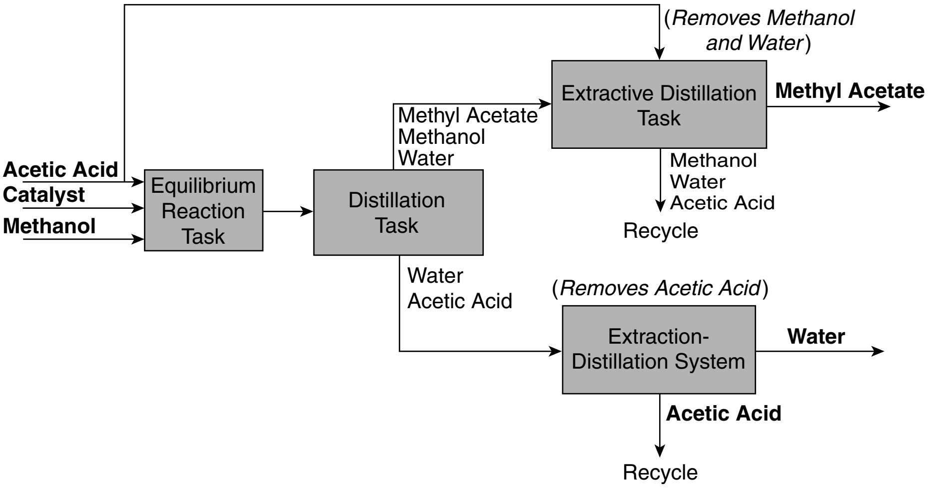


Fig. 10. Methyl acetate process tasks.

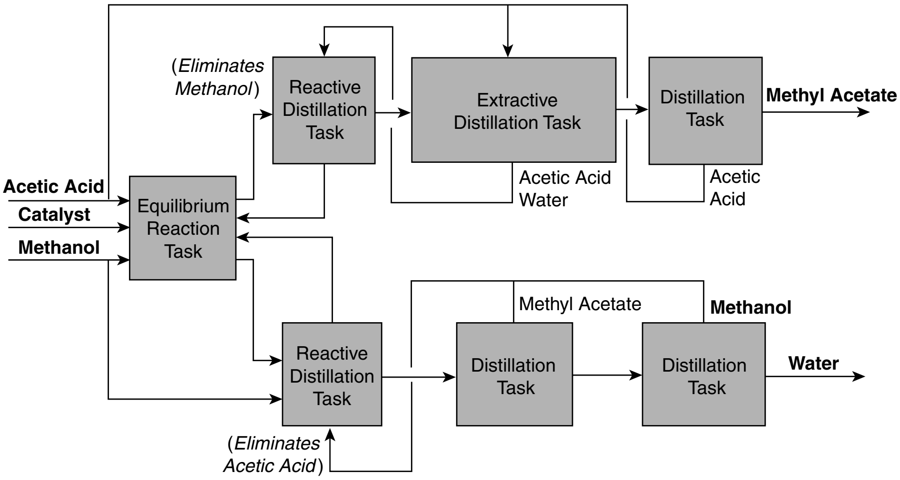


Fig. 11. Methyl acetate process exploiting reactive distillation.

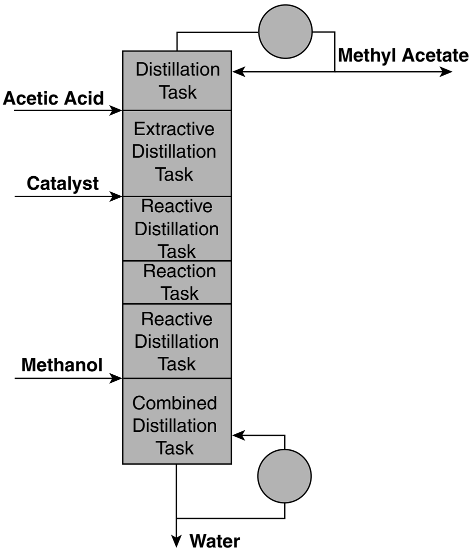


Fig. 12. Integrated one-column methyl acetate process.