

# Synthesis of Separation System Flowsheets

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*A hierarchical decision procedure for the synthesis of separation system flowsheets for vapor–organic liquid–aqueous liquid–solid mixtures is proposed. An expanded set of synthesis rules that can be used to obtain a first design is discussed, but the final goal of the procedure is to generate a complete list of separation alternatives (by changing the decisions) that when coupled with short-cut screening techniques, can be used to identify the best few process flowsheets. The procedure is based on a decomposition of the separation system synthesis problem by phase splitting into a vapor recovery system, a solid recovery system, and liquid separation systems. A general superstructure presented for these subsystems includes all of the common unit operations for petrochemical processes. The procedure focuses on the development of a complete flowsheet for the separation system: which separation system recycle loops (in contrast to reactor system recycle loops) are required, as well as interactions among separation subsystems and those between the separation system and remainder of the process. An example presented illustrates the procedure, and the opportunities for pollution prevention at the source are noted.*

## Introduction

It is essential to develop more competitive processes (better reaction chemistry and better process alternatives), which have less environmental impact. The hierarchical decision procedure of Douglas (1985, 1988) for the conceptual design of chemical processes attempts to identify all of the decisions required to develop a complete process flowsheet. If the way in which various decisions are made is changed, process alternatives are generated. Thus, if the list of decisions is complete (or can be made complete), a systematic procedure for generating all possible alternatives is available. Some decisions (e.g., the addition of water at some point in a flowsheet) correspond to the eventual generation of waste streams. If alternative decisions can be made that eliminate these waste-treatment problems, then the procedure can also be used for waste minimization at the source (Douglas, 1992). This article extends the hierarchical decision procedure to include the synthesis of separation systems for vapor–organic liquid–aqueous liquid–solid mixtures. These separations often exhibit large waste loads.

The established procedures for the synthesis of separation systems are based on list-splitting techniques. That is, a list of the components to be separated and their physical properties (e.g., boiling points, melting points, solubilities in various solvents, etc.) is developed, and then separation techniques that can be used to split the list into smaller lists, and eventually

the desired exit streams, based on the physical properties, as well as the sequencing of these operations, are considered. The most complete set of rules that can be used to implement this approach has been published by Barnicki and Fair for liquid mixtures (1990) and for gas–vapor mixtures (1992).

A proposed taxonomy of separations problems is listed in Table 1. From this taxonomy we see that a complete separation system is obtained from a list-processing procedure only for the case of ideal (or almost ideal) liquid mixtures. For separation operations requiring recycle loops (gas absorption, extraction, etc.), solvent selection, and the specification of the solvent recycle loop is also required to develop a complete separation system flowsheet. Similarly, if crystallization is selected as a separation technique, then it is also necessary to specify the type of crystallizer, a liquid–solid separation system, a cake-washing system, and a dryer system, as well as the destinations of the mother liquor and the cake-washing liquid, which have not been considered in previous articles. Processes where a separation of a mixture of solids or where separation system boundaries are encountered require special flowsheets, which are not obtained from the usual list-splitting procedure. The new decisions that are required to extend the previous work to cases where separation system recycle loops (in contrast to reactor recycle loops) are required are emphasized in this article.

**Table 1. Taxonomy of Separation Problems**

*Systems generated using separation method selection and sequencing based on an ordered list of physical properties:*

- Systems not requiring separation system recycle loops—distillation sequencing of ideal (or almost ideal) liquid mixtures
- Systems requiring separation system recycle loops—gas absorption (solvent selection and recycle), gas adsorption (adsorbate selection and regeneration), extraction (solvent selection and recycle), extractive and azeotropic distillations where there are no distillation boundaries (entrainer selection and recycle), crystallization systems where there are no eutectics (liquid–solid separation selection, cake washing operations, dryer selection, destination of the mother liquor, and the wash liquid), separation of solid mixtures

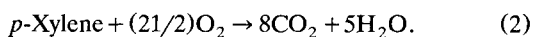
*Problems with separation boundaries requiring special subsystems:*

- Most azeotropic and extractive distillations
- Separation of eutectic mixtures

*Problems where separations are difficult or require special unit operations:*

- Large organic molecules (specialty monomers, pharmaceuticals, ag. chemicals)—pass mixtures to a downstream plant
- Proteins—special unit operations
- Polymers—special unit operations

There are a number of processes where vapor–organic liquid–aqueous liquid–solid mixtures must be separated. For example, in the production of terephthalic acid (TPA) by the air oxidation of *p*-xylene two of the important reactions are:



(A number of other byproducts are also produced.) The reactor exit stream(s) might contain a mixture of gases (unconverted O<sub>2</sub>, N<sub>2</sub>, and CO<sub>2</sub>), organic liquid (*p*-xylene), aqueous liquid (H<sub>2</sub>O), and solid (TPA). The new decisions that are required to extend the list-processing approach to include mixtures of this type are also considered in this article.

The goal of the procedure, when coupled with short-cut screening techniques, is to identify the separation system alternatives that should be considered further. When the rules are applied in a different order or the way in which the decisions are made are changed, different flowsheet alternatives will be generated. The least expensive alternative will depend on the heat exchanger network selected and the optimization of the design variables for the complete process. As the design variables are changed, the best separation system and the best heat exchanger network can change. Terrill and Douglas (1987) demonstrated that when the flows to a process with a specified heat exchanger network are optimized, the energy savings are translated to raw materials savings. It is still desirable to keep the best few flowsheets, however, because the final selection will also depend on safety, operability, and environmental considerations.

## Previous Work

Most of the studies on the synthesis of separation systems has been concerned with the sequencing of ideal distillation columns. As noted in the taxonomy of separation problems given in Table 1, the column sequencing problem provides a complete description of the flowsheet for this case. The list-

splitting procedure has been extended to other separation techniques, including gas absorption, extraction, and crystallization. These articles only consider the separation and the sequencing of various separation operations (alternative tree structures), and do not consider a complete separation flowsheet because the solvent recycle loops normally are not made explicit, that is, the recovery of the solvent is sometimes considered, but the impact of solvent recycle on the separation of subsequent subsystems and the possible interactions encountered in solvent recycle loops are not considered. Distillation separations where separation boundaries are considered have received considerable attention, and solids separations with separation boundaries are under active study. Protein separations have been considered by Siletti and Stephanopoulos (1992), and polymer separation systems have been considered by Malone and McKenna (1990). In these last two cases some of the molecules have much larger molecular weights than those encountered in petrochemical processes, and so special unit operations are required.

## Distillation sequencing for ideal liquid mixtures

There is an extensive literature on the distillation sequencing of ideal liquid mixtures. The first article was published by Lockhart (1947), and then a wealth of articles that include algorithmic, evolutionary algorithmic, and heuristics methods have been published; see, for example, Thompson and King (1972), Gomez and Seader (1976), Westerberg and Stephanopoulos (1975), Seader and Westerberg (1977), Glinos and Malone (1984), and Nadgir and Liu (1988). Heuristics for simple columns and sharp splits, such as lightest first, most plentiful first, cheapest first, favor equimolar splits, and most difficult last, have been discussed by numerous authors. A review of most of this work has recently been presented by Modi and Westerberg (1992), and the various heuristics are compared to a new evaluation criteria, marginal price, which appears to give better results.

The test problems used to develop the heuristics normally considered well-balanced feeds and separations where all of the columns operate at atmospheric pressure. For this reason the difference between the best and the worst sequence is usually less than 50% (Modi and Westerberg, 1992). Very imbalanced feeds to a distillation sequence are common in industrial flowsheets (economics indicates that it is desirable to operate at high conversions for single reactions; economics indicates that only small amounts of heavy byproducts can be tolerated from side reactions; and in many cases a large excess of one reactant is used at the reactor inlet to shift the product distribution). For a process such as butane alkylation, the components include propane, butene, isobutane, *n*-butane, isooctane, and C<sub>12</sub>. With this wide range of boiling points some of the columns must be pressurized, whereas others operate at 1 atm, and the steam temperatures required for the various columns are significantly different. The difference in the costs between the best and worst sequence for these cases can exceed 300%. When pressure differences are encountered, it is always preferable to use costs as an evaluation criterion rather than vapor rate.

Glinos and Malone (1984) found some examples where all of the commonly accepted heuristics predicted the same sequence, but there was a significantly better solution. They

**Table 2. Distillation Column Sequences for Butane Alkylation**

Feed: $x_{C3} = 0.05$ , $x_{i-C4} = 0.696$ , $x_{o-C4} = 0.023$ , $x_{n-C4} = 0.10$ , $x_{i-C8} = 0.10$ , $x_{C12} = 0.05$			
Seq. No.	Cost (10 <sup>6</sup> )	Seq. No.	Cost (10 <sup>6</sup> )
1	24.5	9	73.2
3	26.1	8	73.3
2	26.2	6	74.5
4	39.2	7	76.1
11	42.3	14	90.5
10	43.3	13	90.6
5	43.6	12	92.5

suggested using exhaustive enumeration to calculate the costs of every sequence. Using the short-cut models of Douglas (1988), they developed a code called GIGAS, and with the code it only requires a few seconds on a IBM-PC to calculate all of the sequences for a five-component mixture (which includes most petrochemical processes). This is the procedure that was used by Kirkwood et al. (1988) in PIP. The codes could be made more efficient by replacing the exhaustive enumeration procedure by a branch-and-bound technique (Westerberg and Stephanopoulos, 1975; Gomez and Seader, 1976). However, the exhaustive enumeration results calculated by Malone and Glinos (1990) are interesting, because they indicate that the economics of sequences fall into groups that have about the same costs (see Table 2). Moreover, the best design is indistinguishable from two others.

If the flows are highly imbalanced, somewhere in the sequence it is necessary to separate a dilute binary mixture, which Barnicki and Fair (1990) note is always an undesirable situation. In cases of this type it is better to combine the column with the dilute binary mixture with a neighboring column, and to consider the use of a complex column. Complex columns have been discussed by Tedder and Rudd (1978), Glinos and Malone (1985a,b, 1988), Glinos et al. (1986), and Malone and Nickolaides (1987). Energy integrated distillation sequences (see, for example, Sirola, 1994), and sloppy splits have also been considered.

#### **Separation systems using other techniques or special flowsheets**

A wealth of studies on particular separation operations are available in texts on unit operations, but some additional studies with a process design emphasis have been published (see, for example, Fair (1969) and Keller (1982)). The synthesis of separation systems using other techniques than simple distillation (gas absorption, adsorption, extractive distillation, extraction, crystallization, etc.) have also been studied extensively. Again, both algorithmic and heuristic methods have been considered (see, for example, Thompson and King (1972), Brunet and Liu (1992), Douglas et al. (1993)). The most complete set of rules for liquid separations has been published by Barnicki and Fair (1990), who also published rules for gas/vapor separations (1992). These list processing procedures and specify a separation technique and the sequencing of separation operations, but do not determine complete separation system flowsheets, that is, if crystallization is selected as a separation technique, there is no men-

tion of the need to select the type of crystallizer, a liquid-solid separator, a cake-washing operation, a dryer system, and the destinations of the filter mother liquor or the wash liquid.

Separation boundaries are often encountered in highly nonideal distillation systems, and these boundaries preclude certain types of splits. Rules for determining the feasibility of splits for azeotropic systems have been presented by Foucher et al. (1991). In some cases these boundaries are sufficiently curved that they can be crossed at the expense of large reflux ratios (see, for example, Doherty and Caldarola, 1985). Pressure swing distillation sometimes provides an alternate approach for crossing a boundary. The most common procedure, however, is to add an entrainer that causes a liquid-liquid phase split with compositions in different distillation regions. A procedure for calculating the minimum reflux ratio for nonideal mixtures has been published by Julka and Doherty (1990, 1993). Sequencing for highly nonideal liquid mixtures has been discussed by Doherty and coworkers in a number of articles (see, for example, Doherty and Caldarola (1985), Pham and Doherty (1990), and Julka and Doherty (1993)). Wahnschafft et al. (1991, 1992) have also discussed these problems from an opportunistic planning viewpoint. Industrial examples have been published by Sirola (1995).

Crystallization separations where eutectics are encountered also exhibit separation boundaries, and require special flowsheets. Techniques for separating eutectic mixtures have been published by Rajagopal et al. (1991), Dye and Ng (1994a, b), and Dye et al. (1995). The separation of mixtures of solids has been studied by Rajagopal et al. (1988) and Ng (1991).

#### **Synthesis of complete plants**

The synthesis of complete plants, including separation system for vapor/liquid processes, has been considered by Sirola and Rudd (1971), Sirola et al. (1971), Rudd et al. (1973), Mahalec and Motard (1977a,b), Douglas (1985, 1988), Liu and Motard (1985), Smith and Linnhoff (1988), Kirkwood et al. (1988), and Crowe et al. (1991). The synthesis of processes including solids operations have been discussed by Rossiter and Douglas (1986a,b, 1988) and Rajagopal et al. (1992). Computer codes for the synthesis of complete processes have been developed by Sirola and Rudd (1971), Mahalec and Motard (1977a,b), Liu and Motard (1985), Kirkwood et al. (1988), and Crowe et al. (1991) for vapor/liquid processes, and by Rajagopal et al. (1992) for V/L/S processes. These codes develop a structure of the flowsheet and, except for the codes of Kirkwood and Rajagopal, do not include estimates of equipment sizes or cost calculations.

The PIP code of Kirkwood et al. (1988) is an implementation of Douglas's hierarchical decision procedure (1985, 1988), and it includes a complete set of cost models, distillation sequencing (for ideal mixtures) by exhaustive enumeration, and an evaluation of the process profitability in terms of the dominant design variables (Fisher et al., 1985). Pinch technology (Hohmann, 1971; Gunderson and Naess, 1988; Linnhoff, 1993) was used to estimate the minimum utilities requirements, and the approximate procedure of Townsend and Linnhoff (1984) was used to estimate the capital cost of the heat-exchanger network as a function of the design variables. Terrill and Douglas (1987) showed that when alternative

heat-exchanger networks were added to a flowsheet and the flows were optimized, the apparent energy savings could be translated to raw materials savings, so that the energy consumption increased but the total manufacturing costs often dropped by about 25%. Lam (1989) extended the code to a limited class of plant complexes using the procedure described by Douglas (1990). Rajagopal et al. (1992) developed a similar procedure for solids process, and extended Kirkwood's code to include solids. The goal of the present research was to extend the synthesis procedure to vapor-organic liquid-aqueous liquid-solid separation systems.

## Scope of the Procedure

In the discussion below we consider a set of rules (for the first design) for the synthesis of complete separation system flowsheets and the decisions it is required to make. These results can provide the basis for an expert system that completes a conceptual design (including size and cost calculations) for a particular set of design decisions. Changing these decisions will generate a new process alternative, so that the "best few" alternatives can be identified.

The types of separations considered below include reactor phase splits (flash drums or quench tanks), liquid-solid separators, (thickeners, rotary filters, belt filters, centrifuges, and decanters), gas absorbers, reactive absorbers (with reversible and irreversible reactions), adsorption beds, chilled and refrigerated condensers, membranes, single-stage and counter-current washing for filters and centrifuges (with homogeneous and heterogeneous liquids held up in the cake pores), stripping, distillation column sequencing (ideal mixtures only), aqueous-organic extractions, crystallization (evaporative, flash, indirect cooling, direct cooling, "salting out"), counter-current rotary dryers, cocurrent rotary dryers, and fluid-bed dryers.

Note that only a few examples of liquid-solid separators and dryers are considered. Similarly, many of the gas separation techniques and rules presented by Barnicki and Fair (1990, 1992) are not included. We consider only aqueous-organic extractions, which are the most common in chemicals processes. Nor do we consider azeotropic, extractive, or reactive distillation. (A code to test the feasibility of splits and to design the highly nonideal distillation systems, called Mayflower, is currently being developed by Doherty and Malone (1993), along with several students.) A recent review of reactive distillation has been published by Doherty and Buzad (1992). We assume that each plant in a plant complex will have its own separation system, which is a poor assumption. A procedure is needed for determining the best sequence of distillation columns when there are multiple feed streams. Only the material balance flowsheet is considered, and so heat-exchanger networks need to be added to complete a design.

## Hierarchical Decision Procedure (Revised)

The hierarchical decision procedure (Douglas, 1985, 1988) has been revised to accommodate the new separation system synthesis procedure, as shown in Table 3. The input information required is the same as in Douglas (1988), except that safety and environmental constraints should be added. The rules for determining the number of plants (Level 1 in the

**Table 3. Hierarchical Decision Procedure**

Level	Decision Procedure
0	Input data
1	Number of plants
2	Input/output structure and plant connections
3	Recycle structure
4	General structure of the separation system—phase splits
4a	Vapor recovery system (and gas separations)
4b	Solid recovery system (and solid separations)
4c	Liquid recovery systems
4d	Combine the separation systems for multiple plants
5	Energy integration
6	Evaluate process alternatives
7	Control system synthesis
8	Hazops analysis

procedure) are the same as in Douglas (1990), except plants used to produce or degrade homogeneous catalysts need to be differentiated from plants that carry out the primary reaction chemistry. The decisions for the input-output structure (Level 2) for individual plants are the same, except that a revised list of component destinations given in Table 4 is used. This revised list includes waste streams, so that the wastes generated by the reaction chemistry are identified early in the procedure. For product or byproduct components that are solids at ambient conditions, a decision must also be made whether to remove these streams as crystals, as a melt, as a slurry, or in solution. The component destinations are not unique, and when different destinations are selected, process alternatives are generated.

The connections between plants in a multistep reaction process has been moved to Level 2, but the rules in Douglas (1990) remain applicable. New alternatives can be generated by adding fresh feed reactants in a plant upstream of where they are needed (to act as a solvent, a heat carrier, etc.) or passing mixtures to downstream plants where the separations might be easier (although some of the equipment in the downstream plant must be oversized to accommodate the increased load). Most of the decisions for the recycle structure

**Table 4. Component Destinations**

Noncondensable, gas-phase reactants	Gas recycle and purge or vent to fuel or flare
Noncondensable gas-phase byproducts	Vent to fuel supply or flare
Reactants (condensable gas, liquid, and solid)	Recycle to reactor (or exit)
Reaction intermediates	Recycle to reactor
Homogeneous catalyst	Recycle
Byproducts produced by secondary reversible reactions	Recycle or treat as a byproduct
Feed impurities	Treat as a byproduct
Primary product	Exit to storage
Byproducts	
Valuable byproduct,	Exit to storage
Fuel byproduct	Exit to fuel supply
Waste byproduct	Exit to
	Wastewater treatment
	Incineration
	Landfill
Homogeneous catalyst	Recycle
Homogeneous catalyst activator	Recycle

(Level 3) are the same, except that a reactor-separator should be considered (some reactor recycle streams are eliminated) and operation at a high conversion to avoid a reactant recycle should be made explicit. In addition, if a solid feed stream is supplied to a liquid-phase reactor, either a melter (if the melting point is less than the reactor temperature) or a dissolver usually must be added to the flowsheet. We prefer to use a reactant, a byproduct, or the product as a solvent. If the dissolution kinetics are much faster than the reaction kinetics, the dissolution can be carried out in the reactor.

### Definition of the Complete Separation System Synthesis Problem

The results of Levels 2 and 3 decisions and analyses provide the input information we need for the definition of the separation system synthesis problem: we have estimated the reactor exit flows (the feed to the separation system) and the flows of all of the streams exiting from the separation system and that either exit the process or are recycled back to the reactor (as a function of the design variables). To illustrate the information available for a separation system synthesis problem, we consider a particular example.

#### Example—the production of BHET

The example we consider is an alternative chemical route for making bis (2-hydroxyethyl) terephthalate (BHET), which is the monomer for polyethylene terephthalate (PET). The conventional route for producing this product starts with the air oxidation of *p*-xylene to make terephthalic acid (TPA). The TPA is often converted to dimethyl terephthalate (DMT) because it is easier to purify (a liquid instead of a solid). Then, either TPA or DMT is reacted with ethylene glycol to produce BHET. The BHET can be isolated or directly polymerized to PET. An alternate route patented by Lummus Co. (1969) uses the reaction system below.

##### Plant 1:

$T = 860^{\circ}\text{F}$  ( $460^{\circ}\text{C}$ ),  $P = 26$  psia (179 kPa) Vapor-Solid Reaction

1.  $p\text{-Xyl} + \text{NH}_3 + 3\text{V}_2\text{O}_5 = p\text{-TN} + 3\text{H}_2\text{O} + 3\text{V}_2\text{O}_4$
2.  $p\text{-TN} + \text{NH}_3 + 3\text{V}_2\text{O}_5 = \text{TPN} + 3\text{H}_2\text{O} + 3\text{V}_2\text{O}_4$
3.  $p\text{-Xyl} + 21\text{V}_2\text{O}_5 = 8\text{CO}_2 + 5\text{H}_2\text{O} + 21\text{V}_2\text{O}_4$

##### Plant 2:

$T = 860^{\circ}\text{F}$  ( $460^{\circ}\text{C}$ ),  $P = 26$  psia (179 kPa) Vapor-Solid Reaction

4.  $\text{V}_2\text{O}_4 + 1/2 \text{O}_2 = \text{V}_2\text{O}_5$

##### Rxns 2:

$T = 392^{\circ}\text{F}$  ( $200^{\circ}\text{C}$ ),  $P = 15$  psia (103 kPa) Liquid-Phase Reaction

5.  $\text{TPN} + \text{EG} + 2\text{H}_2\text{O} = 2\text{NH}_3 + \text{BHET}$

where BHET =  $\text{HO}(\text{CH}_2)_2\text{OC}(\text{O})\text{C}_6\text{H}_4\text{C}(\text{O})\text{O}(\text{CH}_2)_2\text{OH}$ ; EG =  $\text{HO}(\text{CH}_2)_2\text{OH}$ ;  $p\text{-TN}$  =  $\text{CH}_3\text{C}_6\text{H}_4\text{CN}$ ; TPN =  $\text{NCC}_6\text{H}_4\text{CN}$ . If the selectivity losses in the ammoxidation process are significantly less than the conventional process and the other costs are also smaller, then the TPN process might be able to displace the TPA process. There is a possibility that the reaction  $2\text{NH}_3 + \text{CO}_2 + \text{H}_2\text{O} = (\text{NH}_4)_2\text{CO}_3$

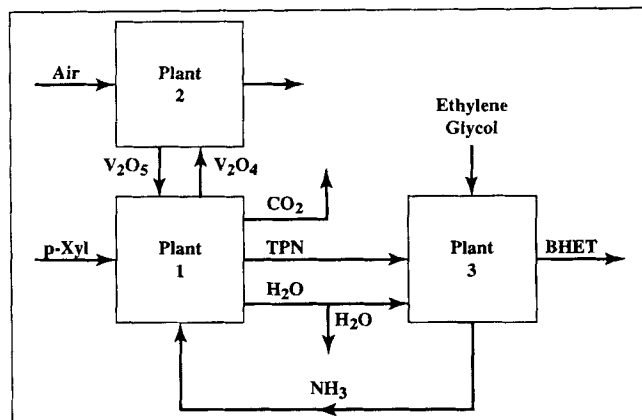


Figure 1. TPN-BHET process plant connections.

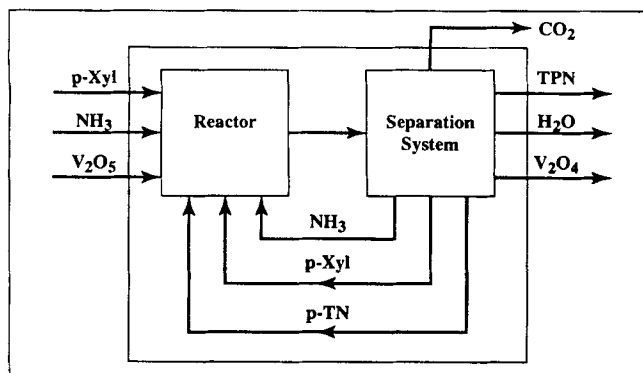
also takes place, although it is not mentioned in the patent. If we design a process ignoring this reaction, and the process is not competitive with the conventional process, we will terminate the design project. If the new process is competitive, however, additional experiments will be needed to determine if this reaction is present.

#### Levels 1 and 2—Input-output structure and plant connections

The rules for multistep reaction processes (Douglas, 1990) indicate that three plants are required, that is, we run reaction 4 in a separate plant because we do not want  $\text{O}_2$  to come in contact with *p*-xylene or the other organics (incompatible chemistry) (see Figure 1). The feed streams to the TPN plant are *p*-xylene,  $\text{NH}_3$ , and  $\text{V}_2\text{O}_5$ , while the exit streams are TPN,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , and  $\text{V}_2\text{O}_4$ . For a first design, we assume that the TPN leaves the process as dry crystals, which corresponds to the patent. The  $\text{V}_2\text{O}_4$  is removed from the fluid-bed reactor separately from the gases and is regenerated in a second fluid-bed reactor (steam stripping of the  $\text{V}_2\text{O}_4$  is necessary to remove the organics adhering to the solid, and this steam addition results in a wastewater treatment problem).

#### Overall material balances

The short-cut techniques of Douglas can be used to estimate the overall and recycle balances, even if the physical properties of all of the components (*p*-TN, TPN) are not known. If the desired production rate is  $250 \text{ lb} \cdot \text{mol/h}$  ( $115 \text{ kg} \cdot \text{mol/h}$ ) of BHET, and if there are no reactant or separation system losses in the BHET plant (a design heuristic indicates that we want to recover more than 99% of all valuable materials, but for a first design we assume 100% recoveries), then from the stoichiometry we see that the byproduct flow of  $\text{NH}_3$  will be 500, and that the required feed rates of TPN is 250, of EG is 500, and of  $\text{H}_2\text{O}$  is 500 (an alternative would be to let some TPN leave the process, because both TPN and BHET are solids at ambient conditions and a TPN-BHET separation might be difficult). Then, if we add the first two reactions in the TPN plant to eliminate the reaction intermediate (which will be recovered and recycled) and if we choose a set of reactor operating conditions [ $x = 0.512$ ,  $T = 860^{\circ}\text{F}$



**Figure 2. Input-output structure and recycle structure of the TPN plant.**

(460°C),  $P = 26$  psia (179 kPa),  $MR_{p\text{-xyl}/p\text{-xyl}} = 3.96$ ], where the selectivities are

$$S_{\text{TPN}/p\text{-xyl}} = \frac{\text{mol TPN produced}}{\text{mol } p\text{-xyl converted}} = 0.952 \quad (3)$$

$$S_{p\text{-TN}/\text{TPN}} = \frac{\text{mol } p\text{-TN formed}}{\text{mol TPN formed}} = 0.238 \quad (4)$$

short-cut overall balances indicate that the  $p$ -xylene feed =  $250/0.952 = 262$ , the  $\text{NH}_3$  feed is 500 (which is equal to the  $\text{NH}_3$  produced in the BHET plant and recycled back to the TPN plant), the  $\text{V}_2\text{O}_5$  consumed = 1,752, the  $\text{CO}_2$  produced is 60, and the  $\text{H}_2\text{O}$  produced is 1,560 (more  $\text{H}_2\text{O}$  is produced in the TPN plant than is required in the BHET plant, so a wastewater treatment problem is encountered), and the  $\text{V}_2\text{O}_4$  produced is 1,752. (A small  $\text{NH}_3$  makeup stream will need to be added later, when separation system losses are considered.)

### Level 3—Recycle structure and flows

The recycle streams in the TPN plant are  $p$ -TN (a reaction intermediate),  $p$ -xylene and  $\text{NH}_3$  (reactants) (Figure 2). Again, using short-cut balances, the  $p$ -xylene fed to the reactor =  $262/0.512 = 512$ , the recycle flow of  $p$ -xylene =  $512(0.488) = 250$ , the recycle flow of  $\text{NH}_3 = 3.69(512) - 500 = 1,389$ , and the recycle flow of  $p$ -TN =  $0.238 \times (250) = 60$ . We use these estimates of the flows (assuming no separation system losses) to synthesize the separation system, and will revise these flows after we have specified a separation system. If we change the reactor design variables (which will change the selectivities), the overall and recycle balances will change. These design variables always correspond to important optimizations.

### Sources of pollution problems

It should be noted that the  $\text{CO}_2$  exit stream from the TPN plant is the source of an air-pollution problem. Similarly, the short-cut material balances indicate that more water is produced in the TPN plant than is needed by the BHET plant, and so a wastewater treatment problem is also present. The stripping steam added for the  $\text{V}_2\text{O}_4$  exit will add to the waste-

**Table 5. Component Type**

A.	Toxic, unstable, corrosive, SARA III
B.	Special reactants—air, water, $\text{Cl}_2$ , $\text{HCl}$
C.	Organics
	1. Organic gases—condensable vs. noncondensable
	2. Organic liquids
	a. Water soluble or not
	b. Monomers
	c. Temperature sensitive
	3. Organic acids—special reactive separation system
	4. Organic solids
D.	Inorganics
	1. Gases—condensable vs. noncondensable
	2. Acids
	3. Salts
E.	Color-forming components
F.	Mixture characteristics
	1. Any explosive mixtures?
	2. Any azeotropes?
	3. Any eutectics?
G.	Anticipate difficult separations
	1. Complete conversion if a reactant and a product
	2. Send to a downstream plant?
	3. Solid product and byproduct—add a purge

water load from the TPN plant, and the exit air stream from Plant 2 is the source of another air-pollution problem. In addition, if dry crystals are removed from the TPN plant, then an additional air-pollution problem will be introduced by adding an air dryer. Other sources of pollution for the TPN plant might also be present as a complete flowsheet is developed, and it is important to keep track of the sources of wastes and to look for alternatives that eliminate these pollution problems.

### Separation System Synthesis

Knowing all of the component flows entering and leaving the separation system defines the separation system synthesis problem. We start the separation system synthesis by adding a new set of component classifications, Table 5, to our component list. We assume that all inorganics we encounter are soluble in water when we consider phase splits. Many of the other classifications are used to set flags on the applicability of distillation separations.

### Level 4a—phase splits

In order to decompose the separation synthesis problem into a set of smaller problems, we first attempt to phase split the reactor exit stream, Level 4a (Douglas, 1985, 1988; Barnicki and Fair, 1992a). For mixed phase organic reactions that contain noncondensable gases (those that boil below propylene) we use the reactor as a phase splitter to remove a vapor stream. If the reactor temperature exceeds 100°F (38°C) (cooling water temperature), we partially condense the reactor vapor stream and phase split it in a flash drum (Douglas, 1985, 1988). The vapor is sent to a vapor recovery system and the liquid is either sent to a liquid separation system or returned to the reactor (a reflux condenser). The liquid leaving the reactor (which may be a liquid/liquid/solid mixture) is usually sent to a filter or a centrifuge to remove the solids, and then to a decanter to phase split the organics from the aqueous liquid, that is, we prefer not to send gases to a filter or a decanter, and we prefer not to send solids to a decanter.

A thickener, that is, a hydrocyclone or a gravity settler, must precede the filter or centrifuge if the solids concentration is less than about 20 to 30 wt.%. Selection rules for thickeners and liquid-solid separators have been published by Purchas (1981) and Ernst et al. (1991). If a gas-solid mixture leaves the reactor, we use a cyclone separator to recover the solids. If a gas-solid mixture is present in a fluid-bed reactor, both a gas and a solid exit stream can be removed (usually it is necessary to strip organics adhering to the solids with steam). This steam stripping eventually leads to a wastewater treatment problem.

For vapor phase reactions, we use a partial condenser (or a quench tank) to cool the gases to 100°F (38°C) (the lowest temperature available with cooling water) and to accomplish a phase split. If the exit stream from the partial condenser is a V/L/L/S mixture, we first remove the vapor in a flash drum, then we remove the solids in a filter or centrifuge, and finally we use a decanter to split the organic and aqueous liquid streams. There are exceptions to this general rule, however, that correspond to new process alternatives. If there is very little vapor and no solids, we can remove the vapors from the remainder of the liquids overhead in a distillation column. If there is very little liquid and no solids, we can recover the liquid in a gas absorber. After vapors have been removed, if there is very little solid it is often better to decant before filtering in order to decrease the load on the filter.

If the reactor exit stream is a homogeneous liquid, we sometimes cool the stream to cause one component to crystallize. In some other cases we add water to an organic stream or an organic to an aqueous stream to cause a phase split and to recover one or more components. Similarly, adding an organic or water to a stream sometimes will cause a component to crystallize. Normally it is cheaper to cause a phase split by cooling, rather than adding a "mass separating agent," because the mass separating agent must be recovered and recycled (unless it is water). If water is used as a mass separating agent and is not recovered and recycled, a wastewater treatment problem is generated.

The vapor leaving a flash drum is sent to a vapor recovery system. The liquid leaving the filter or centrifuge is sent to a solid recovery system, and the organic and aqueous streams leaving the decanter are sent to separate liquid separation systems (Figure 3). We calculate the flows leaving the phase splitters as a function of the reactor design variables. Now the separation system synthesis problem becomes one of synthesizing a vapor recovery system, a solid recovery system, and liquid separation systems. It should be noted that most processes will not contain all of these subsystems, because not all of the phases are present.

### Interactions among the separation subsystems

The individual recovery subsystems are usually interconnected, that is, the solvent required for a gas absorber is recovered and recycled in one of the liquid separation systems, and so forth. Hence, a more complete representation of the flowsheet superstructure is shown in Figure 4. As Figure 4 indicates, the coupling between the subsystems introduces separation system recycle loops into the flowsheet. The purpose of the vapor recovery system is to remove valuable components from an exit gas stream or to prevent toxic compo-

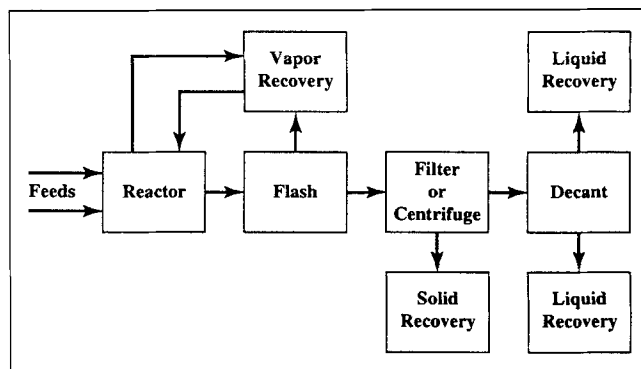


Figure 3. Phase split.

nents from leaving with a gas stream (a gas absorber, a refrigerated condenser with a flash drum, an adsorption bed, or a membrane are the most common techniques that are used). The purpose of the gas separation system is to separate mixtures of gases (cryogenic distillation, pressure swing adsorption, or a membrane are common techniques). However, Barnicki and Fair (1992) note that gas separations are seldom economical unless the exit gas flow exceeds 10 to 20 ton/d.

The purpose of the solid recovery system is to recover valuable materials from the wet cake leaving a filter or centrifuge by washing. The purpose of a solid separation is to separate mixtures of solids, but most industrial processes are designed to prevent the occurrence of such mixtures. The purpose of the liquid separation systems is to separate mixtures of liquids (distillation, extraction, crystallization, and so forth, are common techniques that can be used). Thus, this superstructure includes all of the common separation system techniques.

We consider the synthesis of the vapor recovery system first (Level 4b), because one of the streams leaving this system normally is a liquid mixture that requires separation. We consider the synthesis of the solid recovery system next (Level 4c), because it also produces a liquid stream requiring addi-

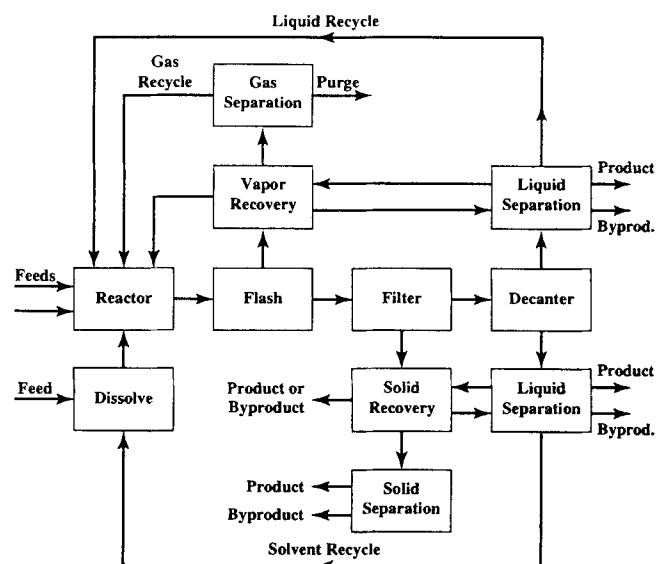


Figure 4. Superstructure for the separation system.

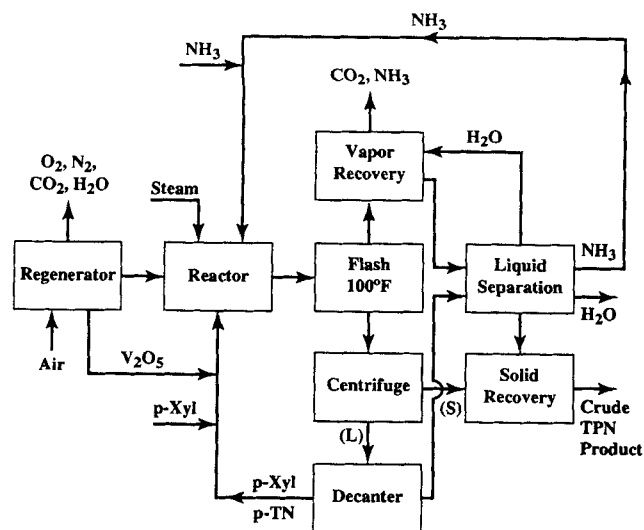


Figure 5. Phase split for the TPN plant.

tional separation. Normally there is no interaction between the vapor recovery system and the solid separation system, but both affect the number of components and the component flows fed to the liquid separation system. The problem definition for the synthesis of the liquid separation system thus might have feeds from the vapor recovery system, the reactor, and the solid recovery system, and it might have exit streams to the vapor recovery system, the reactor, and the solid recovery system, as well as process exit streams. Thus, both the reactor recycle streams and the separation subsystem recycle streams affect the definition of the liquid separation system synthesis problem.

#### TPN plant — Phase splits (Level 4a)

When we cool the gas stream leaving the TPN reactor to 100°F (38°C) in a quench tank (TPN has a triple point above atmospheric, similar to CO<sub>2</sub>, and will form a solid without forming a liquid if cooled below the dew point of the mixture), we obtain a vapor-organic liquid, aqueous-liquid, solid mixture. We remove the CO<sub>2</sub>, and some NH<sub>3</sub> (and H<sub>2</sub>O), in a flash drum, then remove the solid TPN in a liquid-solid separator, and finally split the organics (*p*-XYL and *p*-TN) and an aqueous mixture (H<sub>2</sub>O and NH<sub>3</sub>) in a decanter (Figure 5). The organics can be recycled directly back to the reactor from the decanter without further separation, because it makes no difference if some NH<sub>3</sub> and H<sub>2</sub>O are present in this stream.

This phase split flowsheet is different from the one described in the patent (see Figure 6). In the patent, two quench tanks in series are used that operate at different temperatures, with the final gas stream sent to a vapor recovery system. The L/L/S stream leaving the first quench tank is sent to a centrifuge and then to a decanter. The L/L/S stream leaving the second quench tank is sent to a decanter and the aqueous-solid stream leaving this decanter is sent to the centrifuge. If the two quench tanks were combined and operated at 100°F (38°C), which would reduce the load on the vapor recovery system, and if the L/L/S stream leaving this quench tank was sent to the centrifuge, then a decanter and a recycle loop could be eliminated from the flowsheet shown in Figure 6, and Figure 5 would be obtained.

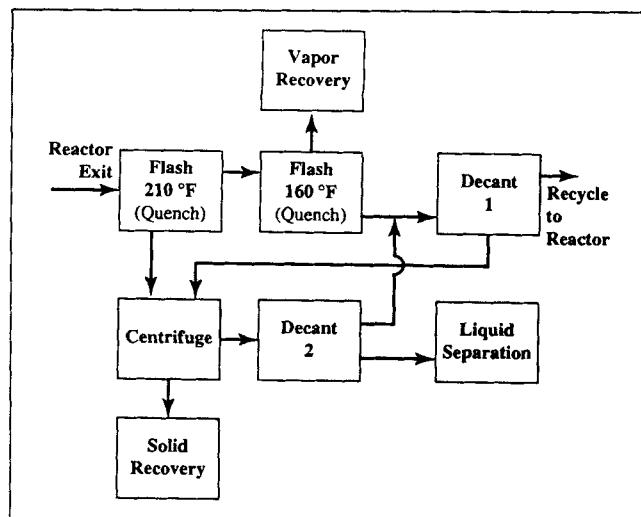


Figure 6. Alternate phase split for the TPN process.

A three-phase flash calculation is needed to determine the flows leaving the quench tank. For a first design we can assume perfect recovery of the TPN in the centrifuge and perfect splits in the decanter. If the process is competitive, we will revise these flows later.

#### Level 4b—Vapor recovery system (and gas separations)

The purpose of a vapor recovery system is to recover valuable components from a vapor stream or to prevent toxic, gaseous components from leaving the process, that is, we remove almost all (more than 99%) of the condensable gases and liquids from noncondensable gases. The common types of vapor recovery units include condensers (high pressure, low temperature, or a combination), gas absorbers, adsorption beds, and membranes. Fair (1969) suggests that adsorption is the least expensive method if the solute composition is less than 5%, but the use of an adsorption bed, with subsequent regeneration introduces a batch operation into the continuous process.

If a process contains a gas recycle and purge stream and if valuable components are lost in the purge stream, the vapor recovery system should be placed on the purge stream because it has the smallest flow rate. If components that degrade the product distribution or foul the catalyst are present, the vapor recovery system should be placed on the gas recycle stream because it has the second smallest flow rate. If valuable components are lost in the purge stream and components that degrade the product distribution or foul the catalyst are present in the flash vapor stream, then the vapor recovery system should be placed on the flash vapor stream. If no components that are valuable, degrade the product distribution or foul the catalyst are present, then a vapor recovery system is not needed.

If a condenser is selected, another flash drum, a refrigeration unit, and/or a compressor must be added to the flowsheet [the original flash drum operates at 100°F (38°C)]. If a gas absorber is selected, a solvent must be selected and the solvent usually must be recovered and recycled. If water is selected as a solvent, it is often sent to a waste treatment facility after the valuable component(s) have been recovered. Hence, the selection of an absorber usually introduces a sep-



aration system recycle loop into the flowsheet. If a component that is not in the reaction system is selected as a solvent, then the solvent may be recovered in a local distillation column (if it is lighter or heavier than all of the other components recovered) or it might be recovered in one of the liquid separation systems. By using a component in the reaction system as a solvent, a distillation separation is saved. If a reactant is used as a solvent, then it is desirable to feed the reactant to the process through the gas absorber because this will allow the absorber to operate at a lower temperature. A first estimate of the solvent flow rate is made using the heuristic that the absorption factor is 1.4, which is valid only for dilute mixtures and isothermal operation.

If a solvent can be found that reacts with the solute, and the reaction can be reversed in a second column to regenerate the solvent (for example,  $\text{CO}_2$  absorption in a number of solvents,  $\text{NH}_3$  absorption in dilute acetic acid-ammonium acetate solution), then a reactive absorption-stripping system is preferred. For the removal of toxic components from a gas stream, a solvent that irreversibly reacts with the toxic component to form a benign material is selected, and the exit liquid mixture is sent to waste treatment.

If an adsorption bed is used, the bed is often regenerated with steam. Fair (1969) suggests that 3 lb of steam/lb of organic are required for regeneration. The exit stream is condensed and the solute and water are usually separated by distillation. It is common practice to send the water exit stream to waste treatment.

Membranes are often used to separate noncondensable gas-phase reactants from other noncondensable gases. For processes with a gas recycle and purge stream, it is usually cheapest to place the membrane on the purge stream. Other gas separation techniques include cryogenic distillation and pressure swing adsorption. According to Barnicki and Fair (1992), gas separations are economical only if the gas flow rate exceeds 10 to 20 ton/d. More details on gas separations are given by Barnicki and Fair (1992).

#### TPN process—Vapor recovery system (Level 4b)

The vapor stream leaving the flash quench tank shown in Figure 5 can be sent to a gas absorber using water (a component in the process) as a solvent to recover most (99%) of the ammonia from the  $\text{CO}_2$ . In order to recover additional ammonia, and to reduce the load on the exit gas treatment system, the gas stream leaving the water absorber can be sent to a second absorber using a dilute acetic acid-ammonia acetate solution. Water (in the gas feed leaving the first absorber) is removed from the top of a second column and is sent to waste treatment. The bottoms of the second column are sent to a third column, where  $\text{NH}_3$  is recovered overhead for recycle to the reactor, and an acetic acid-ammonium acetate solution is regenerated for recycle back to the acid absorber. The  $\text{CO}_2$  exiting the acid absorber still might have to be sent to a flare or an equivalent gas treatment system, depending upon the EPA requirements.

#### Level 4b—Solid separation system (and solid separations)

Whenever a filter or a centrifuge is present in a flowsheet, some valuable liquids usually are held up in the pores of the

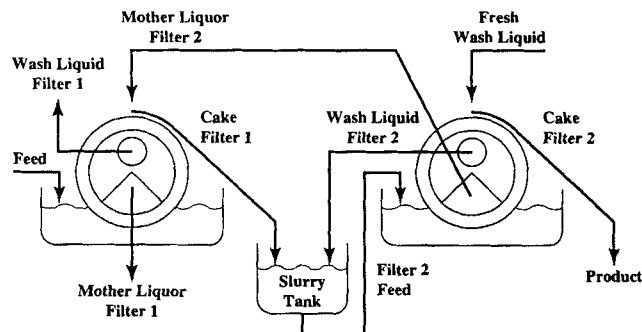


Figure 7. Cake washing for homogeneous liquids.

cake. Cake washing (preferably in the filter or centrifuge) is required to recover these components. For homogeneous liquids and high recoveries, two filters (centrifuges) in series with a countercurrent washing and reslurrying are often used (Figure 7). The new decisions that must be made at this level are the number of washing stages, whether or not to use different wash liquids for multistage washing, the destination of the mother liquor leaving the filter (centrifuge), and the destination of the wash liquid. The amount of liquid retained in the cake can be estimated from the porosity. The amount of wash liquid (usually water) should be determined experimentally, but for rough estimates an amount of wash liquid needed for three displacements of the liquid in the pores can be used.

The valuable components usually are separated from the wash liquid by distillation, and the wash liquid can be recycled. Recycle introduces a new separation system recycle loop into the process. Either a local distillation column can be used or the wash liquid can be recovered in one of the liquid separation systems. The washed cake is normally sent to a dryer. Fluid-bed dryers are restricted to small particles that can be fluidized. Large particles can be dried in a rotary dryer. Cocurrent flow is used for temperature-sensitive materials and countercurrent flow is used otherwise. A large number of other types of dryers are discussed in the literature.

For heterogeneous liquid mixtures held up in the pores of a cake, such as in the TPN process, decanters can be inserted in the washing flowsheet to accomplish a separation. Several examples of these flowsheets are given below.

Solid separations are seldom encountered in petrochemical processes. If crystallization is used to recover a component, usually an attempt is made to prevent any other components from crystallizing. However, if a mixture of solids is encountered, the flowsheets described by Ng (1992) can be used to accomplish a separation.

#### TPN solid recovery system—Cake washing (Level 4c)

The solid recovery system in Figure 5 corresponds to cake washing. In the TPN process the liquid held up in the pores of the cake contains organics (*p*-xylene and *p*-TN) and an aqueous phase ( $\text{NH}_3$  dissolved in  $\text{H}_2\text{O}$ ), so that decanters can be used to accomplish a separation. Early flowsheets for cake washing simply slurried the cake with fresh water (about twice the cake flow to obtain a 33 wt.% slurry) and then washed the cake (three displacements of the liquid). The cake was then slurried again, after which steam passed through the slurry to remove any organics remaining (see Figure 8).

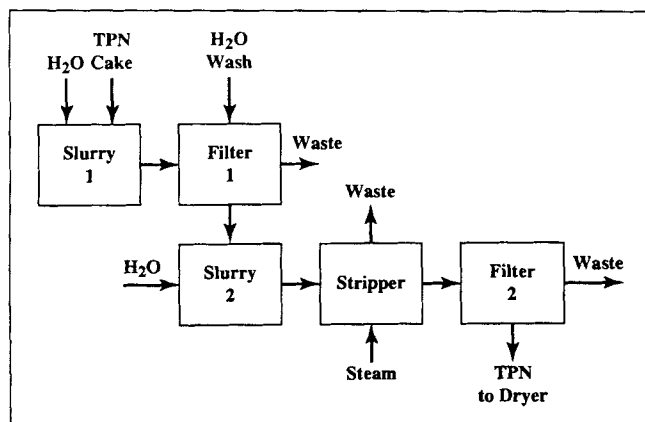


Figure 8. TPN cake washing with no recycle.

Obviously, this configuration corresponds to very large wastewater flows (3.0 lb/lb of BHET product), which we want to avoid.

Another alternative is to use a countercurrent reslurrying flowsheet with decanters to recover the *p*-xylene and *p*-TN (see Figure 9). No washing is carried out in the filters. The wastewater loads for this flowsheet are much less than for that given in Figure 8 (0.05), and the organics recycled back to the reactor reduce the feed requirements for the process.

Another alternative that could be used is to first wash the cake, and then use the wash liquid for reslurrying. Decanters are again used to recover the organics. It might be possible to eliminate decanter 2. This flowsheet requires more water (0.61 vs. 0.11) and gives a higher waste load (0.55 lb/lb) than the flowsheet shown in Figure 10, but less equipment is required.

#### Level 4d — Liquid separation systems

Barnicki and Fair (1990) indicate that distillation is the least expensive technique for separating mixtures of liquids if  $\alpha >$

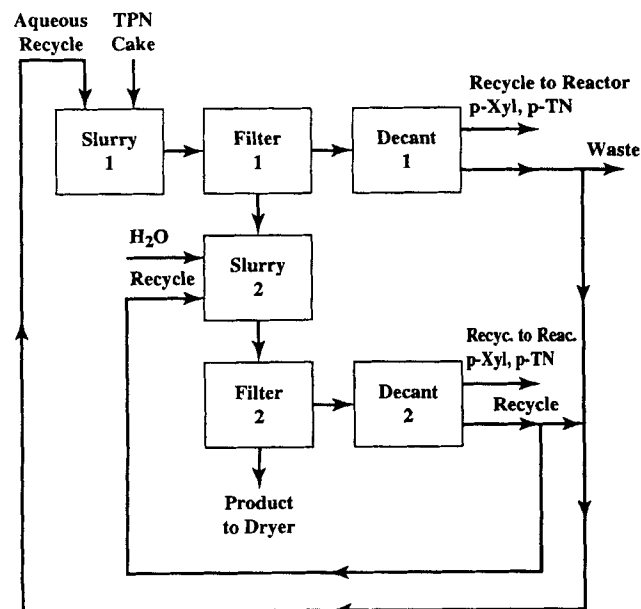


Figure 9. TPN cake washing with reslurrying and decanters.

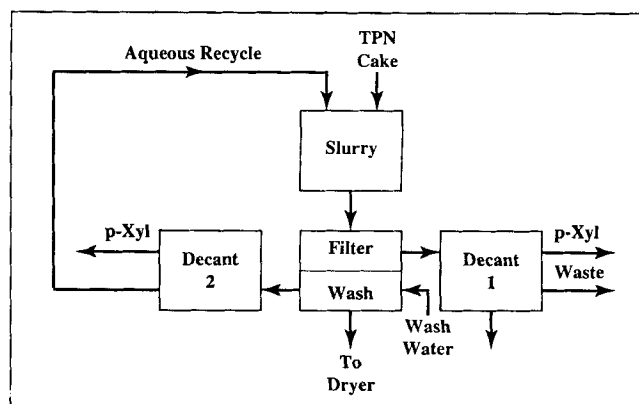


Figure 10. TPN cake washing with decanters.

1.5. In the range  $1.1 < \alpha < 1.5$  other techniques might be competitive, and if  $\alpha < 1.1$  distillation is seldom economical (close boilers). Other techniques should (or must) be considered if there are dissolved noncondensable gases ("light ends"), dilute binary mixtures, tangent pinches (a low  $\alpha$  at one end of a column), dissolved solids, temperature-sensitive components, monomers, organic components dissolved in water, or water-soluble components dissolved in an organic stream. Similarly, if azeotropes are present, distillation separations often are infeasible, and the rules of Foucher et al. (1991) can be used to test for feasibility.

**Stream Purity Specifications.** The purity of the desired product stream and any valuable byproduct streams are part of the original design problem definition. The composition of gaseous vent streams that exit directly to the atmosphere are fixed by EPA requirements. The composition of reactant in a purge stream sent to either a fuel supply or a flare system from a gas recycle and purge loop is fixed by an optimization analysis. The purity of recycle streams is fixed by specifying a recovery of greater than 99% of the reactant. The purity of liquid and solid streams sent to a fuel supply are also fixed using the greater than 99% recovery heuristic. These recovery heuristics are actually approximate solutions of optimization problems where the optimizations are insensitive to the design parameters, but for a first design we use the heuristic value. The final composition of liquid streams sent to waste treatment and of solids streams sent to a landfill are usually fixed by EPA regulations.

**Removal of "Light Ends".** If "light ends" (dissolved, noncondensable gases) are present in a liquid stream leaving a flash drum, and if the lightest (most volatile) liquid component is the desired product or a valuable byproduct, it is usually necessary to remove the light ends in order to meet the purity specification on the product or byproduct. A reboiled stripper (the bottom half of a distillation column), a column with a partial condenser (both a gas exit stream for the light ends and a liquid exit product stream removed from the reflux drum), a pasteurization column (the light ends are removed with a partial condenser at the top of a distillation column and the product is removed as a sidestream five or so trays down from the top), or the use of a stabilizer (a column where the light ends are removed from the reflux drum after a partial condenser, but a significant amount of product is taken overhead to provide reflux) are alternatives that can be considered.

The light ends can be sent to the vapor recovery system or to a fuel supply. If the light ends are sent to the vapor recovery system, a new separation system recycle loop is introduced into the flowsheet. If the lightest liquid component is a reactant, the light ends can be recycled with the reactant. If the lightest liquid component is sent to fuel, the light ends can be left in this stream.

**Stripping with an Inert Gas.** If an inert gas is used to strip light components from a liquid stream, we normally compress the vapor exit stream and send it to a partial condenser and a flash drum. The condensed liquids are sent to their specified destinations or to further separation, and the inert stripping gas is recycled. Hence, stripping with an inert gas often introduces another separation system recycle loop. The recovery is fixed by the product purity and the flow of stripping gas is fixed by letting the stripping factor equal 0.7.

**Distillation Column Sequencing.** If none of the exceptions to distillation need to be considered, and if two components with adjacent boiling points have the same destination, then the components should not be separated by distillation. If close boilers are present, they are lumped together, the best sequence of columns is determined, and then another technique is used to separate the close boilers. If one of the close boilers is a reactant, then the possibility of operating at a very high conversion should be considered to avoid the separation. If the close boilers are isomers, then crystallization should be considered. If the close boilers are from different chemical families or a tangent pinch is encountered, then extraction or crystallization should be considered.

For distillation columns with a single feed stream, Glinos and Malone (1984) recommend that the best sequence of simple columns should be considered first. For mixtures with less than five exit streams (which includes most processes), they found that it takes only a few seconds on an IBM PC to find the best sequence by exhaustive enumeration. They also found cases where all of the sequencing heuristics agree, but do not give the best sequence. For mixtures with more components, a lumping technique or the method of Modi and Westerberg (1992) can be used. Apparently there has been no work on column sequencing with multiple feed streams, which are encountered in many processes or when the separation systems for several plants in a plant complex are combined.

In cases where the component flows are very imbalanced, which is commonly encountered in processes, a dilute binary mixture will be encountered in a simple sequence, and the column will be very expensive. The replacement of this column and a connected column by a complex column should be considered, so that the dilute binary mixture can be avoided. Glinos and Malone (1985) published some useful heuristics for ternary mixtures with unbalanced flows. They and Malone and Nikolaides (1992) also recommend considering the replacement of neighboring columns in all of the possible sequences (or at least the less expensive sequences) by a complex column. They considered 12 types of complex columns and found that it takes only a few seconds to evaluate all of the alternatives. It is interesting to note that the best column configuration, including complex columns for the butane alkylation process (Malone and Glinos, 1990), did not correspond to adding complex columns to any of the least expensive sequences, but to sequence 5 in Table 2, where a 27%

total cost reduction was obtained by replacing the  $n\text{-C}_4/i\text{-C}_8$  split by a "complex, direct" column. When energy integration is considered later, the results might change.

**Temperature-Sensitive Components.** It is desirable not to distill monomers. If a monomer is present in a mixture we prefer to remove it first (or as soon as possible.) If we do decide to use distillation, we use a vacuum column in order to keep the reboiler temperature as low as possible and thereby minimize polymer formation in the reboiler.

If a component decomposes at a temperature lower than its boiling point (e.g., adipic acid), then distillation cannot be used, and another technique (often crystallization or extraction) must be considered. If the temperature-sensitive component is the highest boiler, then stripping of the lighter components with an inert gas followed by condensation and further separation is an alternative.

**Extraction.** We limit our consideration to aqueous-organic extractions, which is a large fraction of the extractions encountered in most chemical processes (not refining). If a mixture is organic, but some components are water soluble, they can be extracted from the mixture into water and then recovered from the water by another separation technique (often distillation or crystallization). The wastewater stream is usually sent to waste treatment.

Similarly, if a mixture is aqueous, but contains some dissolved organics, the organics can be recovered by extraction. An organic solvent must be selected, and it is necessary to recover and recycle the solvent. Thus, the use of extraction introduces another separation system recycle loop. If distillation is used for solvent recovery, either a local column can be used or the solvent can be recovered in the distillation train used to separate the reactant, the product, and other byproducts. If a solvent that is present in the reaction system can be used as a solvent, one less distillation column is required. The exit aqueous stream is usually sent to waste treatment if it contains no additional valuable components.

Extraction units can be either an extraction column, a series of mixer settlers with countercurrent flow of the solvent (which leaves as the extract) and the feed (which leaves as the raffinate), or other types of units. The recovery of the solute is specified to be greater than 99%, and a first estimate of the solvent flow is fixed by setting the extraction factor to 0.7. More complex extraction systems (center feed columns, extractors in series, etc.) are discussed by Cusack et al. (1991), and selection rules for various extractor units have been published by Reissinger and Schroter (1978).

The selection of the solvent can affect the structure of the extraction subsystem. To separate a mixture of acetic acid and water (a mixture that exhibits a tangent pinch at the water end of a distillation column) by extraction, an extraction column and either three distillation columns or two distillation columns and a decanter are required. Sirola (1994) noted that four different solvents (ethyl ether, ethyl acetate, isobutyl acetate, and octyl acetate) are representative of solvents that are used commercially by different companies, and that the flowsheet subsystems for each solvent are different (the different solvents have different distillation residue curve maps, and therefore the best connections between the extraction column and the distillation columns or decanter are different). Thus, solvent selection requires more than just a consideration of physical properties.

**Crystallization.** If crystallization is selected as a separation technique, it is also necessary to add a liquid–solid separator, a cake-washing system, and a possibly a dryer after the crystallizer (these have been discussed previously). If the desired product or a valuable byproduct is a solid at ambient conditions but is dissolved in a liquid mixture, then crystallization is normally chosen. We prefer to remove the solid component before any distillation operations. If a component is a liquid at ambient conditions, but is a close boiler or is temperature sensitive, and if its melting point is fairly high (greater than  $-20^{\circ}\text{C}$ , according to Barnicki and Fair (1990)), then crystallization should be considered. If a crystallizer is used to recover a component that is a liquid at ambient conditions, the crystals are melted after they have been filtered and washed. Similarly, after crystallization and recovery of the solids, the solid is often melted so that it can be pumped to a downstream process. Other alternatives include removing the solid as a slurry or in solution.

**Type of Crystallizers.** There are a number of different types of crystallizers that can be considered, including evaporative crystallizers, flash crystallizers, direct-cooling crystallizers, indirect-cooling crystallizers, and “salting-out” crystallizers. Evaporative and flash crystallizers are used when it is desirable to remove solvent (usually water) from the mixture. Evaporative crystallizers are used when the solid component is not very temperature sensitive, and flash crystallizers (operating under vacuum) are used when the solid component is temperature sensitive. Indirect cooling crystallizers (with a cooling jacket or cooling coils) are used when the solubility decreases with temperature and cooling water or a refrigerant is adequate. Direct cooling crystallizers, where a liquefied gas such as ethylene is added, are used when very low temperatures are required. If the slurry obtained from a cooling crystallizer is less than 20 to 30 wt.% solids, then the use of an evaporative or flash crystallizer will avoid the need for a thickener. Salting-out crystallizers are used when the addition of water or an organic has a significant effect on the solubility and will cause a component to crystallize.

**Number of Crystallization Stages.** Normally crystallizers are operated at only 3 to 5% in excess of saturation, that is, at close to equilibrium conditions. If highly supersaturated conditions are used, the crystals grow too rapidly and often trap pockets of solution inside of a solid particle (inclusion). If inclusion takes place, then high purities cannot be obtained by cake washing. Thus, in order to obtain high recoveries of the solute, a number of crystallization stages are required, similar to a multieffect evaporator. A filter or centrifuge is used to remove the solids between crystallization stages when the solids concentration is in the range from 20 to 50 wt. %.

In situations where eutectics are not present (the eutectic composition is  $<1\%$ ) and we can recover most of the solute ( $>99\%$ ), a single crystallizer with a mother liquor recycle and purge stream around the liquid–solid separator, two crystallization systems and liquid–solid separators in series with 90% of the solute recovered in the first system and 90% of the remainder in the second, or two crystallizer systems and liquid–solid separators in series with a mother liquor recycle and purge stream around both crystallizers are alternatives of interest. The purge streams are often sent to waste treatment. The alternative destinations of the solids are discussed below.

For mixtures that exhibit eutectics, separation system boundaries are encountered. In these cases pure crystals can be obtained along with a liquid mixture at the eutectic composition in a single crystallizer. When the eutectic is a mixture of isomers (usually formed by reversible reactions), the eutectic mixture can be sent to a separate isomerization reactor (*p*-xylene and *m*-xylene mixtures) or recycled to the plant reactor. Otherwise, mixtures at the eutectic composition can be separated by the extractive distillation flowsheets of Rajagopal et al. (1991) or Dye and Ng (1994b), the temperature swing method of Dye and Ng (1994b), or the techniques described by Ng (1991) and Dye et al. (1994) for separating mixtures of solids. Special flowsheet subsystems are required for these systems.

**Crystallizer System Flowsheets (Recrystallization).** If two crystallizers are used, the washed solids recovered from the filters (centrifuges) can be combined and sent to a dryer, while the mother liquor from the second filter is recycled back to the first crystallizer (with a purge stream) or somewhere upstream of the first crystallizer. Another alternative is to use a sedimenting centrifuge after the second crystallizer and to recycle a liquid–solid slurry back to the first crystallizer. With this approach, the solids entering the first crystallizer act as seeds for additional crystallization, and often larger particles can be obtained (which are easier to filter). In cases where very pure solid products are required, it is often necessary to redissolve and to recrystallize the product. The mother liquor leaving the filter after the recrystallization step can be recycled to the first crystallizer in the separation system. Another alternative is to add a recycle and purge stream around each crystallization subsystem.

**Crystal Structure—Effect of Impurities.** It is well known that crystal shapes can be very sensitive to impurities. A very small change in an impurity concentration can change the crystal habit from a cubical structure to a needlelike structure. Similarly, in some cases the solids may resemble popcorn. Since the filtration and washing characteristics can change dramatically if the habit changes significantly, a careful experimental program and a careful design are required. In addition, it is necessary to pilot all solids processes with recycle streams, since an attempt to avoid a pilot program almost always leads to an inoperable process.

#### **TPN process—liquid separation system (Level 4d)**

The only liquid mixture that needs to be further separated in the TPN process is the ammonia–water mixtures leaving the first  $\text{NH}_3$  absorber and the decanter. This separation can be carried out in a distillation column, with the overhead  $\text{NH}_3$  recycled back to the reactor, part of the water recycled to the gas absorber and part sent to waste treatment.

#### **Other Alternatives and Waste Minimization for the TPN Process**

The flowsheet described in the patent sends all the water that is produced by the reaction and the stripping steam used for the exit  $\text{V}_2\text{O}_4$  stream to waste treatment, and supplies fresh water to the BHET process. However, if the  $\text{NH}_3$ – $\text{H}_2\text{O}$  distillation column is designed to give a high purity water exit stream, part of this water can be recycled to the absorber, part could be used as a feed stream to the BHET plant, and

the remainder sent to waste treatment. The water leaving the distillation column could also be used for cake washing of the TPN. This alternative significantly reduces the waste load from the combined process (a 23% waste load reduction). In addition, even though the washing flowsheet shown in Figure 10 requires more water than the flowsheet shown in Figure 9, no additional pollution load is encountered (and less equipment is needed) if the water is reused.

One of our original assumptions is that we would recover dry crystals from the TPN plant, and then supply these to the BHET plant. The crystals are soluble in ethylene glycol, and the dissolution kinetics are sufficiently fast that the solid can be dissolved in the BHET reactor. Thus, an alternative would be to dissolve the TPN cake in ethylene glycol, and transfer the TPN between plants as a solution (any water left in the cake that is in this solution can be sent to the BHET plant, because water is a reactant in that plant). This alternative requires the addition of a dissolver in the TPN plant, but eliminates the need for a dryer in the TPN plant and a screw feeder in the BHET plant.

Another alternative would be to transport the TPN crystals to the BHET plant as a water slurry (providing that both plants are built on the same site and are close together, that is, no storage of TPN is required), since water is a reactant in the BHET plant. It should not matter if small amounts of  $\text{NH}_3$  are present in this stream, since  $\text{NH}_3$  is a byproduct of the BHET reaction. This alternative adds another slurry vessel to the flowsheet, but again eliminates the need for a dryer and a screw feeder. Dryers also are the source of air-pollution problems, so the use of a solution or slurry transfer system would eliminate another air-pollution problem at the source. This type of pollution prevention alternative should be added to the list of the sources of pollution problems generated by Douglas (1992).

Opportunities for pollution prevention at the source by considering process alternatives should always be considered. One advantage of the hierarchical decision procedure is that it makes all of the decisions required to specify a flowsheet explicit, and process alternatives can be generated by changing some of these decisions. Most companies are very reluctant to reuse water in a process because trace contaminants might build up in recycle loops or affect the reactions in downstream plants. Thus, careful consideration of the destination of trace components is essential (Joshi and Douglas, 1992), and experiments must be carried out to test this exit stream as a feed for the BHET process.

### Economic Potential at Level 4

Our goal is to estimate the economic potential of the process including the separation system as a function of the design variables, where the economic potential is defined as

$$\begin{aligned} \text{EP}_4 = & \text{Product value} + \text{byproduct values} - \text{raw material costs} - \\ & \text{annualized capital and operating cost of a feed or recycle} \\ & \text{compressor} - \text{annualized capital and operating cost of the reactor and a melter or dissolver} - \text{annualized capital and operating cost of the vapor recovery system} - \text{annualized capital and operating cost of the solid recovery system} - \text{annualized capital and operating cost of the liquid separation system.} \quad (5) \end{aligned}$$

It is important to note that the "best" separation system can change as the design variables change. For example, for the complex reactions where only a distillation train is needed to separate the unconverted reactants, the product and the byproducts, at low conversions (low selectivity losses) there will be a large reactant recycle stream, whereas at high conversions (high selectivity losses) the reactor recycle stream will be very small. Thus, the load on the distillation train can change significantly, and the best distillation sequence can change.

It is also important to note that even though the economic potential will exhibit optimum values as a function of the design variables for the process with a specified separation system, the value of the optimum will change when a heat exchanger network is added. That is, the recycle costs will change and therefore the optimum flows will change (Terrill and Douglas, 1987). Hence, the "best" separation system cannot be determined until after the energy integration problem has been considered.

### Conclusions

A hierarchical decision procedure has been presented for the synthesis of separation system flowsheets for vapor-organic liquid-aqueous liquid-solid processes starting with the component flows leaving the reactor and the specified component destinations and flows leaving the separation system. The decisions required to specify a separation are made explicit, and by changing these decisions, process alternatives will be generated. The procedure first decomposes the separation system synthesis problem into a number of subsystems (a vapor recovery system, a solid recovery system, and an organic and an aqueous liquid separation system) by phase splitting the reactor exit stream (the reactor may also be used as a phase splitter).

The synthesis of the vapor recovery system and the solid recovery system are considered first, because there is little interaction between these two subsystems, but both change the definition of the liquid separation subsystem problem (they can change the number of components and their flows). Separation system recycle loops, in contrast to reactor recycle loops, are normally encountered between the subsystems and within the subsystems. It appears as if there are a very large number of decisions that need to be made and alternatives that need to be considered. However, the chemical and physical constraints associated with any particular reaction system make it possible to efficiently prune the search space. Process alternatives that eliminate the source of pollution problems were also considered.

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