Synthesis of Processing System Around a Crystallizer

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A systematic procedure is developed to synthesize the processing system upstream and downstream of a crystallizer. In a step-by-step manner, the procedure guides the user to generate alternative flow sheets for treating a given crystallizer effluent. It consists of five steps. The required unit operations are determined by comparing the product specifications (production rate, product purity, and others) with the crystallizer effluent characteristics (occlusions, inclusions, crystal size, and others). Secondly, the destinations of the reaction solvent, mother liquor, wash liquid, recrystallization solvent, and drowning-out solvent are assigned. Third, the solvent recovery system is considered to recover the solvents and unconverted reactants and to remove the impurity from the system. Fourth, alternatives for enhancing process performance are identified. Finally, short-cut models are used to screen process alternatives. Rules and heuristics are provided for each step, and examples for illustrating this procedure are presented.

Introduction

Crystallizers do not exist in isolation in a processing plant. A preconcentrator may be present upstream, and filtration, washing, dewatering, and drying steps are often required downstream of a crystallizer. How such auxiliary equipment functions individually has been discussed extensively in the context of solid–liquid separation processes (Purchas, 1971; Svarovsky, 1981; Purchas and Wakeman, 1986) and industrial crystallization (Bamforth, 1965; Mullin, 1993). In contrast, how to integrate these units to form an optimal crystallization system has received only scant and sporadic attention. For example, Jones (1985) pointed out that problems in solid–liquid separations often arise and benefit from control of the upstream crystallizer. Rossiter and Douglas (1986) studied the optimization of a salt plant, focusing on the evaporative crystallizer, downstream centrifuge, and fluid-bed dryer. They found that the crystal size can be constrained by the mother liquor entrainment limit of the crystallizer, and that the crystal size affects the residual moisture content in the centrifuge and, thus, the drying cost. Similarly, for a potash plant, Rajagopal et al. (1988) found an optimal dominant crystal size which depends on a tradeoff between the crystallizer cost and the filter cost.

While potential improvements were proposed for the specific plants in these previous investigations, most of the generic design issues have not been adequately addressed. For example, consider crystal washing. A number of solvents may be present in the plant, including reaction solvent, drowning-out solvent (also referred to as antisolvent) and recrystallization solvent. Can one of the existing liquid streams be used for washing, or is fresh wash solvent preferred? In some cases, it is adequate to wash the crystals in the filtration unit such as a centrifuge or a rotary vacuum filter; in other instances, countercurrent two-stage washing is beneficial. How do all of these decisions affect the overall flow sheet structure? The objective of this study is to address these questions by providing a systematic procedure for the synthesis of the processing system around the crystallizer. This constitutes part of our overall effort on the synthesis and simulation of solids plants (Rajagopal et al., 1992; Hill and Ng, 1997) and the synthesis of crystallization processes (Dye and Ng, 1995; Berry et al., 1997).

New Procedure for Crystallizer Subsystem Synthesis

The following scenario is assumed in developing the synthesis procedure. The reaction system, if used before the crystallization step, is assumed to be known and fixed. Based on laboratory and bench-scale tests, decisions have been made on the crystallizer type and operating conditions. Data are available on the crystal-size distribution, magma density, and

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Table 1. Evolutionary Procedure for the Synthesis of a Pre- and Post-Crystallization Processing System

Step 1: Selection of the Required Unit Operations
Step 2: Assignment of Solvent Destination
Step 3: Solvent Recovery System
Step 4: Process Enhancement
Step 5: Evaluation of Flow Sheet Alternatives

inclusion and occlusion impurity concentrations. The product purity and production rate, as required by the business, are also known. The task at this stage of process development is to design a flow sheet for the system around the crystallizer for processing the crystals and mother liquor. It is assumed in this article that no attempts will be made to redesign the crystallizer(s) in order to change its effluent characteristics. Drying is not included in this procedure because, normally without a recycle stream, the dryer can be treated as a stand-alone unit.

As Table 1 indicates, the procedure consists of five steps. Step 1 specifies the characteristics of the crystallizer effluent stream and the product specifications. This sets the targets and determines the required unit operations for the process to be synthesized. In Step 2, the required equipment units are connected by recycle streams involving the unconverted reactants, reaction solvent, drowning-out solvent, recrystallization solvent, and wash solvent. Exit points for impurities are also identified at this stage (Joshi and Douglas, 1992). Step 3 considers the solvent recovery system where solvents are recovered and impurities are removed. In Step 4, alternatives for enhancing process performance are considered. Then, Step 5 screens the flow sheet alternatives using shortcut models. The decisions to be made at each step, and the companion heuristics and calculations are now described below.

To provide a more concrete description, the procedure is discussed alongside a simplified adipic acid process. A complete plant involves two major reaction stages (Kroschwitz and Howe-Grant, 1991a). First, cyclohexane is oxidized with air to form the intermediates cyclohexanol ($C_6H_{11}OH$) and cyclohexanone ($C_6H_{10}O$), usually referred to as KA oil. Then, the mixture (60 mol % cyclohexanol and 40 mol % cyclohexanone) is oxidized with nitric acid, followed by a crystallization step to recover the product. The reaction solvent, nitric acid, is recovered and recycled. Glutaric acid ($HO_2C(CH_2)_3CO_2H$) and succinic acid ($HO_2C(CH_2)_2CO_2H$) are major impurity byproducts. For simplicity, only the nitric acid reactor and the subsequent crystallization system are considered in this example. The glutaric and succinic acids are lumped together as one impurity. The conversion and selectivity are assumed to be fixed. Values of the input parameters for this process are listed in Table 2. Other examples for illustrating the procedure are given at the end of this article.

Step 1: Selection of Required Unit Operations

Input information related to the reactor and crystallizer has to be provided by the user in this step. A generic flow sheet is shown in Figure 1. For the reaction system with a feed F, the composition of the reactor effluent stream (stream 2) needs

Table 2. Values of Input Parameters for Adipic Acid Process

Product Specifications		
Production Rate (based on dry adipic acid)		25,000 (kg/h)
Impurity Level (kg impurity/kg dry adipic acid)		50 ppm
Moisture Content (kg solvent/kg dry adipic acid)		0.1%
Reaction System		
Temperature		70°C
Conversion of KA Oil		100%
Net Consumption of HNO_3		0.92 kg/kg adipic acid
Water Generation		0.23 kg/kg adipic acid
Mass Ratio HNO_3/KA Oil at Reaction Feed		7
Concentration of HNO_3 at Reaction Feed		50 wt. %
Selectivity (basis: 1 mol KA Oil Converted)		
Adipic Acid		0.92 mol/mol KA Oil
Glutaric Acid		0.08 mol/mol KA Oil
Crystallization System		
Crystallizer Type		Vacuum
Temperature		50°C
Composition of the Primary Crystallizer Effluent		
Solid Phase		
Adipic Acid		25,000 kg/h
Inclusion Impurity		100 kg/h (~ 400 ppm)
Liquid Phase		
Adipic Acid		24,258 kg/h
Glutaric Acid		34,460 kg/h
HNO_3		113,943 kg/h
Water		105,143 kg/h
Typical Cake Porosity		0.4
Empirical Wash Constant (a)		−1.1
Solubility Values		
At crystallizer temperature	Adipic Acid	0.23 kg adipic acid/kg water
	Glutaric Acid	0.5 kg glutaric acid/kg water
At dissolver temperature	Adipic Acid	1.5 kg adipic acid/kg water
	Glutaric Acid	2.5 kg glutaric acid/kg water

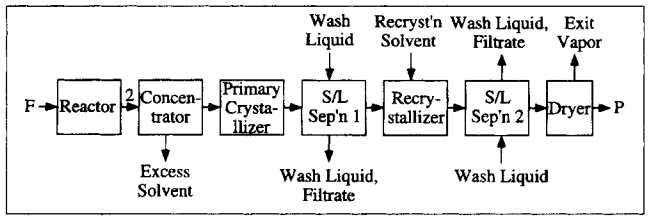

Figure 1. Generic flow sheet structure in Step 1.

to be specified. The crystallizer type such as a drowning-out crystallizer or an evaporative crystallizer determines whether a drowning-out solvent feed stream or an evaporated solvent effluent stream is needed. If reactive crystallization takes place, the reactor and crystallizer can be combined as one single unit. We have the following guideline:

Rule 1: Use a crystallizer after the reactor to be referred to as the primary crystallizer to obtain the product (P) as a solid if reactive crystallization does not take place in the reactor. If it does, only the reactor is used.

If the reactor effluent is very dilute, the crystallizer may not be able to handle the stream effectively. Removal of some of the solvent with a concentrator between the reactor and the primary crystallizer can reduce the heating or cooling load for the crystallizer. Thus, we have

Rule 2: Use a mother liquor preconcentrator such as an evaporator between the reactor and the primary crystallizer if the product concentration in the reactor effluent is excessively dilute.

Filtration is usually used to recover the solids from the crystallizer effluent. If the filter cake contains inclusion impurity (or any other modes of impurity incorporation which are not amenable to removal by a reasonable amount of washing) or the crystal size and shape need to be improved, a recrystallization step is used next. In such a step, the filter cake is dissolved in the recrystallization solvent, and then the solution is sent to the recrystallizer. Adsorbents such as activated carbon may be used in the dissolution tank to remove color forming agents. In that case, a filter is used between the dissolution tank and the recrystallizer to remove the solids.

Rule 3: A recrystallization step is needed if (a) the crystal qualities such as size and shape do not meet the product requirements or (b) the amount of impurity inclusions after the primary crystallizer is greater than the purity requirement.

The solids cake obtained in the filtration step contains the reaction solvent in its pores. If the recrystallization solvent is different from the reaction solvent, a washing step is used in the solid–liquid separation system before the recrystallization step to perform solvent switching. In such a step, the reaction solvent is replaced by the recrystallization solvent so that it will not affect the crystal quality during recrystallization.

Rule 4: If the recrystallization solvent is different from the reaction solvent, use a wash unit to perform solvent switching. This would also help minimize the propagation of the reaction solvent downstream.

Another purpose of washing is to reduce the occlusion impurity. Generally, dissolved impurities are present in the mother liquor. By replacing the liquor trapped in the void space with relatively pure wash liquid, the impurity content in the solids is reduced. However, a significant amount of trapped mother liquor can also be removed by vacuum, pressure, and gas-blowing dewatering. If dewatering alone is sufficient to meet the purity requirement, washing may not be necessary.

Rule 5: A wash unit is needed in the solid–liquid separation system, but before the dewatering step, if dewatering is insufficient to remove the occlusion impurities.

If the trapped mother liquor in the first solid–liquid separation system still contains valuable reactants that are difficult to recover from the solvents, consider using two wash units in series. Using makeup or purified reaction solvent as the wash liquid in the first wash unit, the liquid effluent containing the valuable reactants is recycled to the reactor. The filter cake is then sent to the second wash unit and washed with a different wash liquid. Thus, we have

Rule 6: If residual cake moisture contains valuable reactants that are difficult to recover downstream, consider washing the filter cake with the reaction solvent and recycling it to the reactor.

Step 1 for Adipic Acid Process. The flow sheet is given in Figure 2. Since reactive crystallization does not take place in the reactor (R) (Table 2), a vacuum crystallizer (C1) is needed after the reactor (*Rule 1*). The reaction produces a significant amount of water. An evaporator (CON) is used between the reactor and the primary crystallizer to concentrate the dilute reactor effluent (*Rule 2*). The inclusion impurity level after the primary crystallizer, 400 ppm, is higher than the product specification of 50 ppm. Thus, a recrystallization step is necessary to remove the inclusion impurity (*Rule 3*). Since the recrystallization solvent (water) is different from the reaction solvent (nitric acid), a wash unit for solvent switching (W1) is used before the recrystallization step (*Rule 4*).

Thus, the flow sheet consists of a reactor, a preconcentrator, and a primary crystallizer, followed by a washing step for solvent switching. In the recrystallization step, crystals are dissolved in a dissolution tank (DS) followed by a filter (F2) to remove the activated carbon. Recrystallization takes place in a crystallizer (C2), which is followed by a filter (F3) to recover the solids product. Another wash unit (W2) is used after the filter to wash off the occlusion impurity from the filter cake before the dewatering step (*Rule 5*). After dewatering (DW), the wet crystals are dried in a dryer (DRY).

Step 2: Assignment of Solvent Destination

After determining the required units, the interconnections among these units are constructed by assigning the stream destinations. A generic flow sheet for step 2 is shown in Figure 3. A number of solvents may be involved in the crystallization process, including reaction solvent, drowning-out sol-

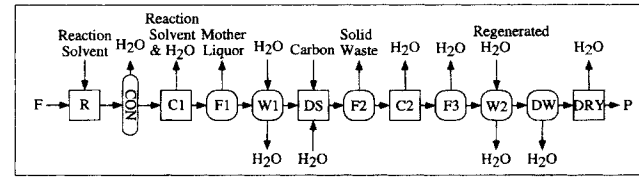

Figure 2. Flow sheet configuration for adipic acid process in Step 1.

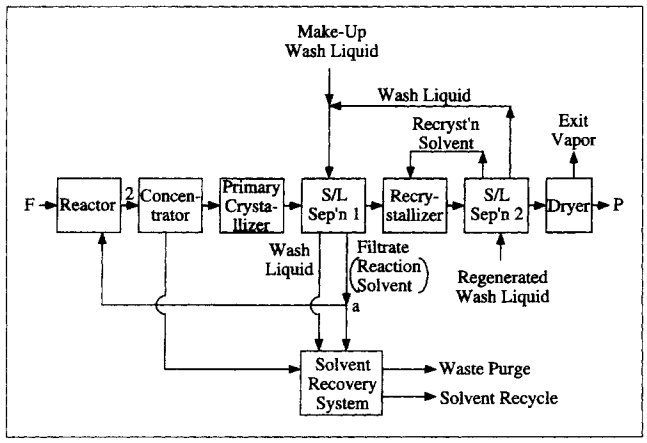

Figure 3. Generic flow sheet structure in Step 2.

vent, recrystallization solvent (also referred to as the dissolution solvent), and wash solvent. The reaction solvent is often fixed by the reaction requirements whereas the recrystallization solvent is selected based on its effects on nucleation and growth, and crystal quality. To minimize the load for the solvent recovery system, the way in which the filtrate (reaction solvent) after the primary crystallizer is split (point a in Figure 3) and the destinations of the resulting streams play a significant role.

Rule 7: Recycle the maximum amount of filtrate after the primary crystallizer to the reactor provided that the level of accumulated impurity does not cause any problems for the reaction nor for the crystallization.

Rule 8: Send the rest of the filtrate after the primary crystallizer to the solvent recovery system for impurity removal since the impurity concentration is the highest in this stream.

The following rules are based on the observation that the level of impurity in the product should decrease along the processing train.

Rule 9: Send fresh or regenerated wash liquid to the last wash unit, because it would provide the highest purity to the final product.

Rule 10: Consider using the liquid effluent stream from a downstream unit as a solvent for an upstream unit such as a reactor, a dissolution tank, or a wash unit. The impurity level in the downstream liquid may be sufficiently low to be reused for the upstream unit.

Figure 3 shows that the wash liquid from the last solid–liquid separation system is reused as recrystallization solvent, and the filtrate is reused for washing in the solid–liquid separation system upstream.

Rule 11: If there are two or more upstream units that can use a downstream solvent and/or two or more downstream liquid effluent streams suitable for reuse upstream, the different combinations of receiving units and supplying streams constitute process alternatives.

Rule 12: If a liquid effluent stream cannot be used for any other upstream units, send that effluent stream to the solvent recovery system to recover the solvent and remove the impurity.

The crystallizer type has a strong influence on solvent recycles. The following rules reflect the potential effects.

Rule 13: A mixed solvent with the solute soluble in one cosolvent but relatively insoluble in the other is often used in drowning-out crystallization. If such a crystallizer is used for the recrystallization step, consider combining the liquid streams from two different sources to obtain a drowning-out solvent concentration with which the product is selectively crystallized.

Rule 14: If the solvent is removed in an evaporative crystallizer, the effluent mother liquor can be recycled to the crystallizer for complete recovery of the dissolved product.

Rule 15: The mother liquor from the cooling or evaporative crystallizer effluent stream can be recycled to the reactor or dissolver to replenish the amount of dissolved product.

Rule 16: For seeded crystallizers, consider recycling part of the solid product from the downstream solid–liquid separation system to the crystallizer.

Step 2 for Adipic Acid Process. The flow sheet configuration in this step is shown in Figure 4. The destination of each stream can be determined as follows. Regenerated wash liquid is used for the last wash unit (W2) (*Rule 9*). Since the wash liquid can be used as the dissolution solvent, the effluent streams from W2 and the dewatering step (DW) are sent to the dissolution tank (DS) to be reused as the dissolution solvent (*Rule 10*). The evaporative solvent from the recrystallizer (C2) mainly consisting of wash liquid is sent to the last wash unit (*Rule 9*). The filtrate from filter 3 (F3) is sent to the first wash unit (W1) as wash liquid since the impurity concentration in that filtrate is lower than that of the trapped liquor in the filter cake (*Rule 10*). The liquid effluent from W1 is then sent to the evaporator (CON) to recover the wash liquid; in other words, the evaporator also serves as part of the solvent recovery system (*Rule 12*). Note that, at 1 atm, nitric acid-water forms a maximum boiling azeotrope at 120°C and 69 wt. % HNO_3 (Kroschwitz and Howe-Grant, 1991b). The filtrate from the first filter (F1) consists of impurity byproducts, solvents, and a small amount of product. Part of it is recycled back to the reactor, and the rest is sent to the liquid separation system to remove the impurity (*Rules 7 and 8*). The evaporative solvent from the crystallizer (C1) consisting of nitric acid and water is recycled back to the reactor (*Rule 10*).

Step 3: Solvent Recovery System

Solvent recovery system is considered in this step (Figure 5). The goal is to recover the solvents (reaction solvent, recrystallization solvent, drowning-out solvent, and wash liquid) and unconverted reactant, and to remove the impurity from

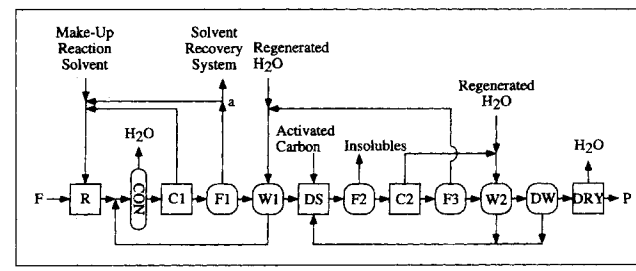

Figure 4. Flow sheet configuration for adipic acid process in Step 2.

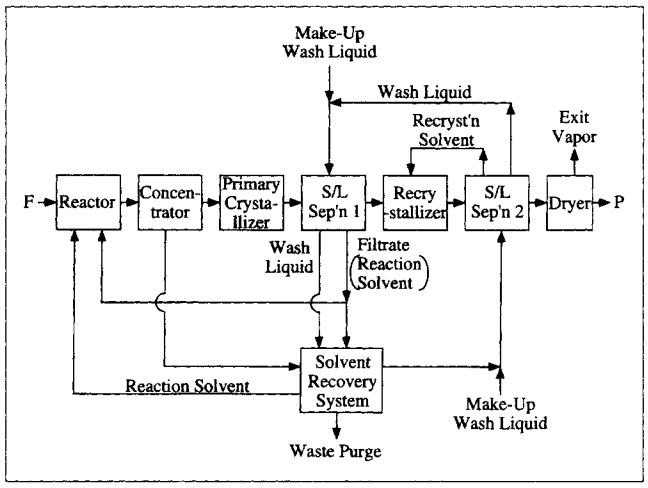

Figure 5. Generic flow sheet structure in Step 3.

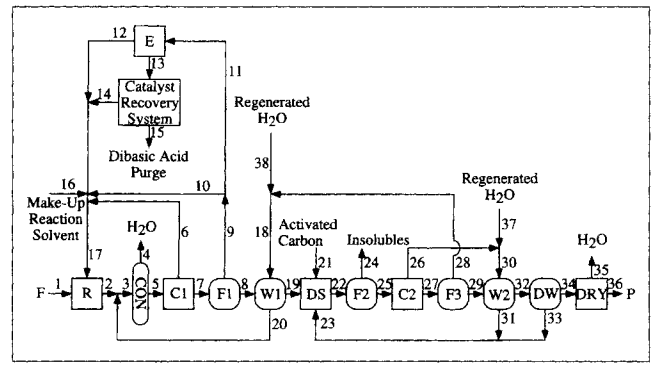

Figure 6. Flow sheet configuration for adipic acid process in Step 3.

the process. The number of feed streams to the solvent recovery system is known after Step 2. The next step is to determine the number of effluent streams from the solvent recovery system. First, we classify all the components in the solvent recovery system effluent streams as shown in Table 3.

Then, rule 17 is applied to determine the number of effluent streams. It is based on the fact that it would be a waste to separate two components and then send them to the same destination.

Rule 17: Order the components by the order of separation and lump the neighboring components of the same destination together. The number of effluent streams is the number of lumps.

For example, if ideal distillation is used as the separation technique, the order of separation can be the same as the order of the normal boiling points. Figure 5 shows three exit streams from the solvent recovery system. Clearly, if the wash liquid for the last wash unit is different from the recrystallization solvent, the number of the exit streams would increase by one.

Some solvent is expected to leave the process with the solids product and/or impurity, and the reaction solvent might be consumed in the reaction step. Make-up solvents are needed to compensate for these losses. However, the impurity purge stream should be concentrated to minimize solvent loss.

Rule 18: It is often not economical to completely recover the solvents in the solvent recovery system, but the impurities should be concentrated before purging.

Table 3. Component Destinations for Solvent Recovery System

Component	Destination
Reaction Solvent	Reactor
Recrystallization Solvent	Dissolution Tank
Drowning-Out Solvent	Crystallizer/Recrystallizer
Wash Liquid	Last Wash Unit
Product	Exit
Reactant	Reactor
Impurity	Exit

Step 3 for Adipic Acid Process. The flow sheet configuration in this step is shown in Figure 6. The solvent recovery system has one feed stream (Stream 11) but three exit streams (*Rule 17*). An evaporator (*E*) is used to recover the water and nitric acid, and an ion-exchanger serves as the catalyst recovery system to reclaim the catalyst. The recovered water, nitric acid, and catalyst are sent back to the reactor via Streams 12 and 14. The purge stream (Stream 15) contains mainly dibasic acids and a small amount of solvent (*Rule 18*). The water recovered in Stream 4, if sufficiently pure, can be used as regenerated water for Streams 37 and 38.

Step 4: Process Enhancement

Steps 1 to 3 provide an overall flow sheet structure. Alternatives can be considered at this point to enhance process performance. For example, consider the filtration and dewatering steps in the flow sheet. The choice of filter equipment based on slurry density and particle size has been discussed elsewhere (Rajagopal et al., 1992). Detailed ranking systems have been proposed by Purchas (1971). However, there are three interesting alternatives from a systems perspective:

Rule 19: Consider the use of countercurrent washing if the washing efficiency is relatively low. While the extra filter and tank incur additional costs, the amount of wash liquid required can be reduced considerably.

Rule 20: If the mother liquor slurry density after a crystallizer is relatively dilute, consider using a slurry preconcentrator before a filter/centrifuge. For example, a combination of hydrocyclone and filter/centrifuge may be cheaper than filter/centrifuge alone.

Rule 21: Choosing between a filter and a centrifuge can be based solely on the feed slurry characteristics. However, a rotary filter generally provides a higher washing efficiency and, thus, uses a smaller amount of wash liquor. This in turn implies a considerably lower load for the wash liquid recovery system.

Step 4 for Adipic Acid Process. Flow sheet alternatives can be generated based on the rules provided in this step. Figure 7 is generated based on *Rules 19 and 20*. The highlighted hydrocyclone/centrifuge combination and countercurrent washing can be attractive depending on the operating conditions. The best configuration is determined by evaluating the economic potential of each alternative.

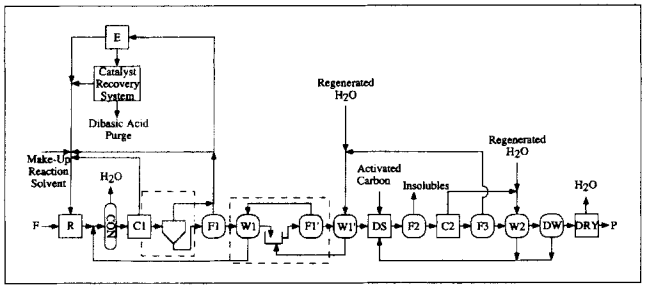

Figure 7. Flow sheet alternative for the adipic acid process in step 4.

Step 5: Evaluation of Flow Sheet Alternatives

By now, a complete flow sheet as well as process alternatives are generated. To evaluate the flow sheet, the design equations are derived by applying appropriate mass balances. Three balances related to washing in a crystallization downstream processing system are described below.

Washing involves the displacement of the liquor in the filter cake by a wash liquid. The amount of wash liquid used in washing step is usually expressed as a ratio of the volume of wash liquid used to the volume of liquor in the cake, referred to as the wash ratio or number of displacement N. When washing is over, the fraction of impurity remaining in the cake f can be obtained by the following empirical equation

$$f = \frac{C_I(\text{out}) - C_I(W)}{C_I(\text{in}) - C_I(W)} = e^{aN} \tag{1}$$

where C_I(out) (kg solute/kg solvent) is the impurity concentration in the wash liquid after washing and is the same as that inside the washed cake, C_I(in) (kg solute/kg solvent) is the impurity concentration in the slurry feed, C_I(W) (kg solute/kg wash liquid) is the impurity concentration in the wash liquid before washing, and a is an empirical constant. More detailed models based on the dispersion coefficient can be found in the literature (Wakeman, 1980). Equation 1 can be used for three specific cases of washing.

Single-stage washing

Refer to Figure 8a. Let C_I(out) be the maximum impurity concentration in the washed cake and pure wash liquid be used for washing. Rearranging Eq. 1 yields the wash ratio for single-stage washing

$$N = \frac{1}{a} \ln\left(\frac{C_I(\text{out})}{C_I(\text{in})}\right) \tag{2}$$

Two-stage countercurrent washing

Refer to Figure 8b. The wash ratios for first and second stage are

$$N_{CC} = \frac{1}{a} \ln\left(\frac{C_I(2)}{C_I(\text{in})}\right) \tag{3}$$

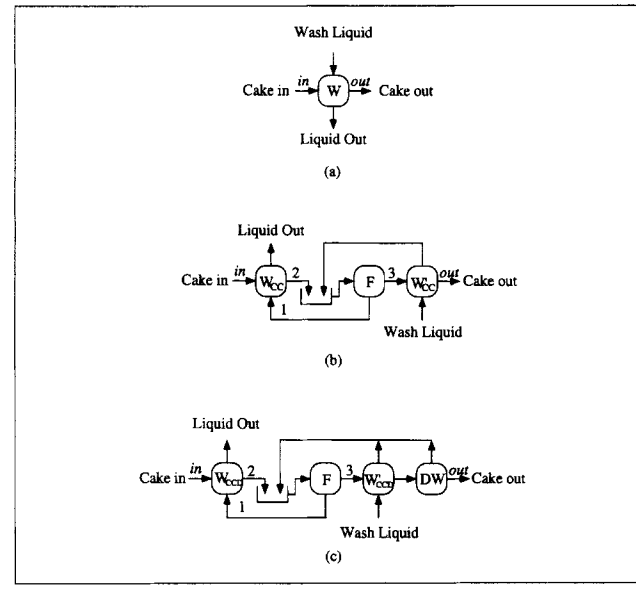

Figure 8. (a) Single-stage washing; (b) two-stage countercurrent washing; (c) two-stage countercurrent washing with dewatering.

$$N'_{CC} = \frac{1}{a} \ln\left(\frac{C_I(\text{out})}{C_I(3)}\right) \tag{4}$$

The numbers in parentheses are the stream numbers in Figure 8b. For two-step countercurrent washing, $N_{CC} = N'_{CC}$. To minimize N'_{CC} is equivalent to maximizing $C_I(3)$. Note that $C_I(3)$ is always less than or equal to $C_I(2)$, because the impurity concentration downstream should be lower than the impurity concentration upstream. Therefore

$$[C_I(3)]^2 \le C_I(2)C_I(3) = C_I(\text{in})C_I(\text{out}) \tag{5}$$

A maximum value of $C_I(3)$ corresponds to an equality in Eq. 5. The corresponding wash ratio is given below

$$N_{CC} = \frac{1}{2a} \ln\left(\frac{C_I(\text{out})}{C_I(\text{in})}\right) \tag{6}$$

Thus, the amount of wash liquid used in two-stage countercurrent washing is approximately half of that in single-stage washing.

Two-stage countercurrent washing with dewatering

Refer to Figure 8c. Assume that the fraction of the mother liquor trapped in the pores to be dewatered is f_{DW}. Then, the difference between the first wash ratio and second wash ratio will be f_{DW}, that is, $N_{CCD} - N'_{CCD} = f_{DW}$. Similar to the previous derivations, a minimum value of N_{CCD} is obtained when

$$C_I(3) = \sqrt{e^{af_{DW}} C_I(\text{in})C_I(\text{out})} \tag{7}$$

and

$$N_{CCD} = \frac{1}{2a} \ln \frac{C_I(\text{out})}{C_I(\text{in})} - \frac{f_{DW}}{2} \tag{8}$$

Thus, the wash ratio can be further reduced by $f_{DW}/2$ in this case.

In deriving the countercurrent washing equations, an implicit assumption is that the impurity concentration of the filtrate from the filter $C_I(1)$ is sufficiently low that it can be neglected. If $C_I(1)$ is high, the wash ratio obtained from Eq. 8 can serve as a lower bound and the actual amount of wash liquid can be obtained by iteration.

Along with the material balances around the other processing units, the flow rate and composition in each stream of the flow sheet at steady state can be determined. Short-cut models for the rotary drum vacuum filter, hydrocyclone, and centrifuge have been developed for screening the economic potential of each flow sheet.

Step 5 for Adipic Acid Process. Some of the key material balance equations are given below. Refer to Figure 6 for the stream numbers. One of major design variables in this flow sheet is the mother liquor recycle fraction f_{ML}. The value of the mother liquid recycle fraction is related to the rate of impurity generation during the reaction G_I (kg/h)

$$F_T(9)C_I(9)(1 - f_{ML}) = F_T(11)C_I(9) = G_I \tag{9}$$

From an overall material balance, G_I is also equal to the amount of impurity to be purged. Some of the adipic acid is also purged along with the impurity as product loss

$$\text{Product loss} = F_T(9)C_P(9)(1 - f_{ML}) \tag{10}$$

Equations 9 and 10 show that mother liquor recycle fraction f_{ML} impacts three factors—the load to the solvent recovery system $F_T(11)$, the product loss due to purge, and the impurity concentration in the crystallizer $C_I(9)$. Furthermore, the impurity concentration in the crystallizer effluent affects the amount of wash liquid required downstream. All these contribute to the fact that the mother liquor recycle fraction is an important design variable.

To achieve solvent switching, the wash ratio for the first wash unit N_1 is usually fixed. Assume that at least 99.5% of the reaction solvent entering into the first washing stage has to be removed during washing and that the empirical wash constant a equals -1.1. From Eq. 2, $N_1 = 5$ for single-stage washing and, from Eq. 6, it is approximately 2.5 if two-stage countercurrent washing is used at W1.

The minimum amount of the dissolution solvent for the dissolver is

$$F_W(23) = \frac{F_P(19)}{S_P} - F_W(19) \tag{11}$$

where S_P is the solubility of adipic acid (kg solute/kg solvent). The wash ratio for the second wash unit with single-stage washing N_2 is obtained from the following equation

$$N_2 = \frac{1}{a} \ln \left(\frac{C_I(32)}{C_I(29)} \right) \tag{12}$$

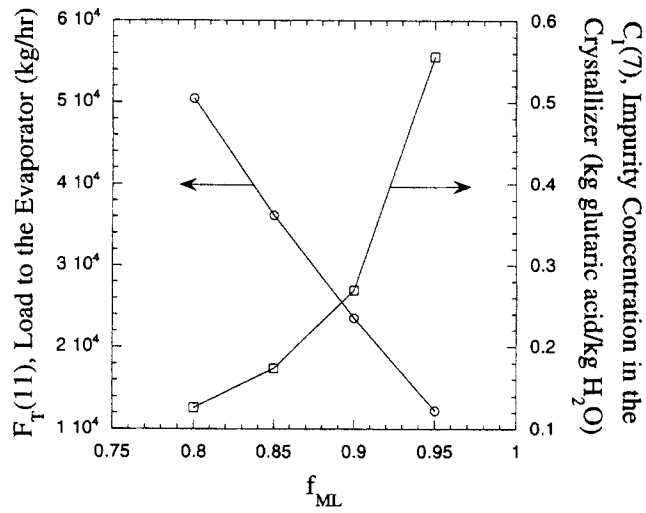

Figure 9. Effects of mother liquor recycle fraction on load to the solvent recovery system and impurity concentration in the crystallizer.

In this example, we assume that 85% of the liquid in the pores will be removed during the dewatering step: that is, $f_{DW} = 0.85$. Detailed dewatering models for different methods of dewatering are available in the literature (Wakeman, 1979; Carleton and Salway, 1993). For given product specifications (production rate, maximum impurity concentration, and moisture content), these balances along with the material balances around the reactor, preconcentrator, crystallizers, filters, and dryer can be used to determine the composition and flow rate in each stream.

Results and Discussion

As discussed, one of the important design variables is the mother liquor recycle fraction f_{ML}. The effect of f_{ML} on the load to the evaporator and the impurity concentration in the crystallizer is shown in Figure 9. When f_{ML} increases, the load to the evaporator $F_T(11)$ decreases; on the other hand, the impurity (glutaric acid) concentration in the crystallizer $C_I(7)$ increases. This is because more of the mother liquor from the primary crystallizer is recycled back to the reactor instead of going to the evaporator (E). When the impurity concentration builds up, coprecipitation of glutaric acid may occur. Therefore, we should keep f_{ML} as high as possible to minimize the evaporator operating cost, but not higher than the point for the coprecipitation of glutaric acid. Ideally, the glutaric acid concentration in the crystallizer should be close to its saturation point for the most economical flow sheet. However, note that the level of impurity concentration can affect the habit and shape of the adipic acid crystals.

Figure 10 shows the effect of f_{ML} on the product loss (Eq. 10) in the dibasic acid purge stream and the impurity level in the final product. When f_{ML} increases, the product loss in the purge decreases because the flow of the purge stream decreases. However, Figure 10 also shows an elevated impurity level in the final product. This is expected since the impurity concentration increases as f_{ML} increases. With the same amount of wash liquid downstream in the process, there

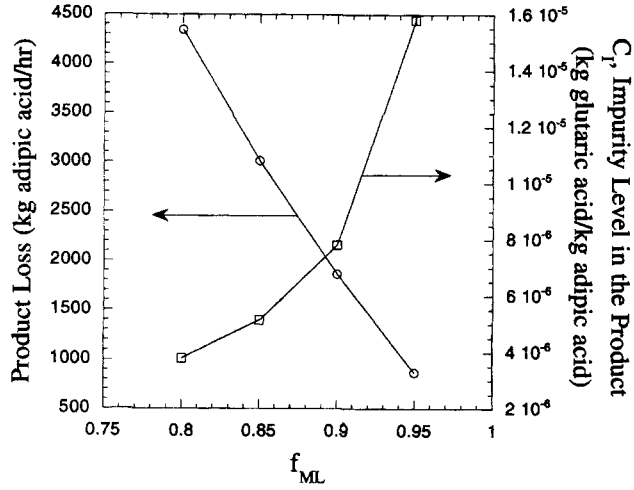

Figure 10. Effects of mother liquor recycle fraction on product loss and impurity level in the product.

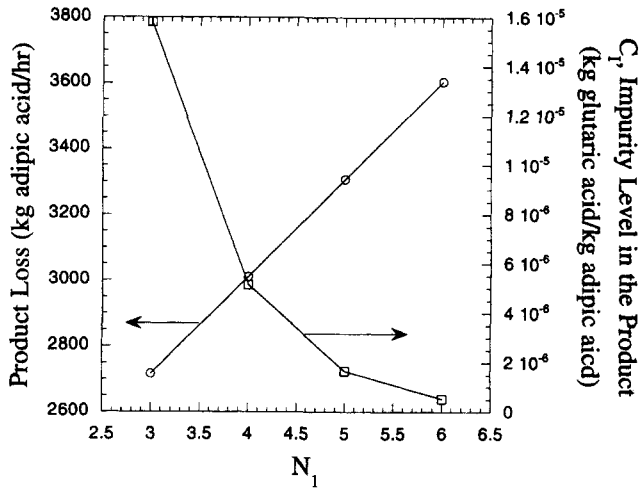

Figure 12. Effects of wash ratio N_1 on product loss and impurity level in the product.

will be more impurity left in the final product. Since there is a maximum allowable impurity level in the product, the maximum value of f_{ML} can be limited by cocrystallization of the impurity in the crystallizer or by the maximum amount of impurity in the product.

Figure 11 shows the impact of the wash ratio for the first wash unit N_1 on the upstream evaporator and crystallizer. As N_1 increases, $F_T(20)$ increases and the load to the evaporator $F_T(11)$ increases while the impurity concentration in the crystallizer $C_I(7)$ becomes more dilute. Figure 12 shows the effect of N_1 on the product loss in the dibasic acid purge stream (Stream 15) and the impurity level in the product (P). As N_1 increases, the product loss increases because the purge stream flow increases. The impurity level in the final product C_I decreases; more impurity is washed away with additional wash liquid.

Figure 13 shows the effect of the wash ratio for the second wash unit N_2 on the downstream recrystallizer and the impurity level in the final product. The latter decreases as N_2 increases, because more impurity is washed away with additional wash liquid. On the other hand, the recrystallizer load $F_T(25)$ increases because of the additional wash liquid from W2 to the dissolution tank. In general, we want to use as little wash liquid as possible. However, one has to use more than a minimum amount of solvent with which all solids from upstream can be dissolved (Eq. 11).

As discussed, the wash ratio can be reduced by half with two-stage countercurrent washing. The impact on the process between single-stage washing and two-stage countercurrent washing has been compared for the adipic acid plant. Figure 14 shows a reduced load to the solvent recovery system with countercurrent washing for W1 (see Figure 7). Figure 15 shows the corresponding impact on product loss in the dibasic acid purge stream. The flow sheet with countercurrent

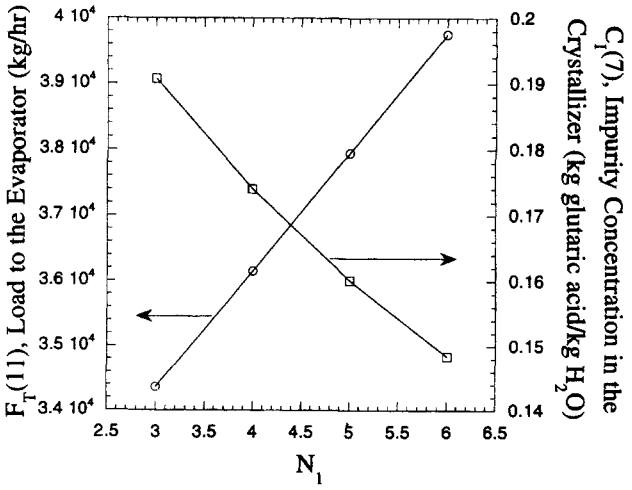

Figure 11. Effects of wash ratio N_1 on load to the solvent recovery system and impurity concentration in the crystallizer.

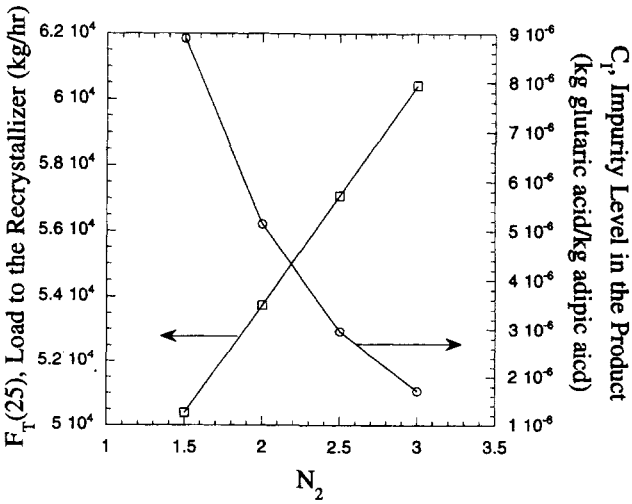

Figure 13. Effects of wash ratio N_2 on load to the recrystallizer and impurity level in the product.

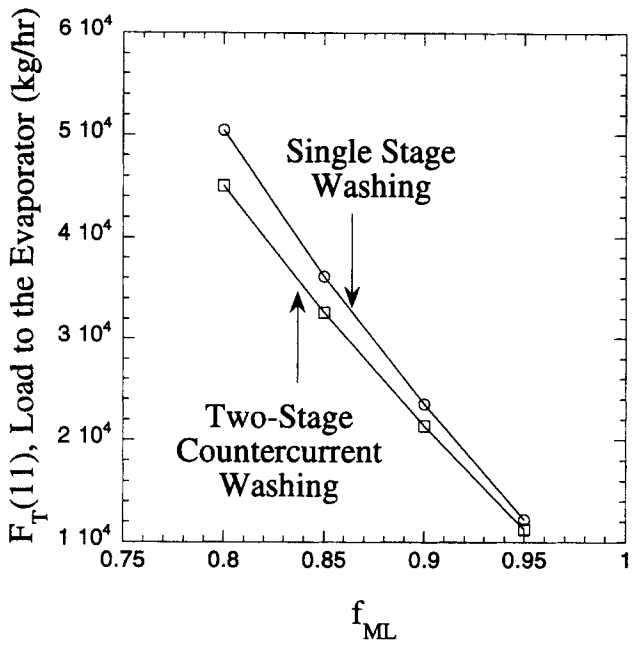

Figure 14. Comparison of the load to the solvent recovery system between use of single stage washing and two-stage countercurrent washing for solvent switching.

washing has less product loss, because the total load to the solvent recovery system is reduced. Both figures show that the difference between single-stage and two-stage countercurrent washing diminishes as f_{ML} increases. That is, if the process can be operated at a high value of f_{ML}, there is not much incentive to use countercurrent washing. However, if f_{ML} cannot be operated at such a high value due to cocrystallization or other reasons, the flow sheet with countercurrent washing becomes attractive.

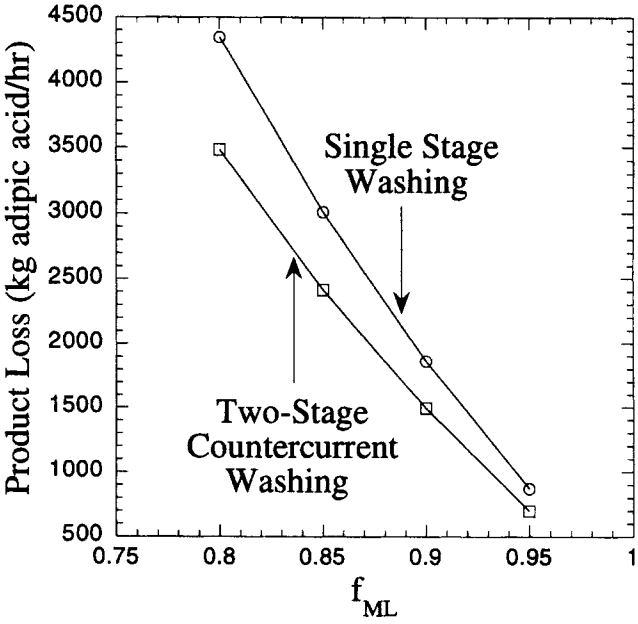

Figure 15. Comparison of the product loss between use of single-stage washing and two-stage countercurrent washing for solvent switching.

Additional Examples

Additional examples are presented to demonstrate how to apply the proposed procedure for synthesizing a base-case flow sheet for a crystallization processing system.

Example 1: Cellulose triacetate process

The reaction system of the cellulose triacetate (CTA) process involves a feed tank where cellulose and glacial acetic acid are mixed (Kroschwitz and Howe-Grant, 1991c). This is followed by the acetylation reactor where cellulose reacts with acetic anhydride to produce cellulose triacetate and acetic acid. During acetylation, some of the sulfate groups attach to the hydroxyl groups in the glucose units so that these hydroxyl groups are not replaced by acetyl groups. These sulfate groups are removed in a saponification reactor by reacting with the water in an 80% acid stream. The acetylation reaction is stopped by the addition of water to convert the excess acetic anhydride to water. The CTA product is recovered by drowning-out crystallization. To precipitate the acetate in powder form, 4% acetic acid solution is added to the crystallizer.

Flow Sheet Generation. The flow sheet configuration constructed in step 1 is shown in Figure 16a. From the input information, the reactor system is followed by a drowning-out crystallizer (C) to recover the solids product. A filter (F) is used to recover solids from the crystallizer effluent. A wash unit is used after the filter to wash off the occlusion impurity from the filter cake (*Rule 5*). This is followed by the dewatering and drying steps. In addition to wash liquid, the liquid effluents from W and DW also contain a minute amount of acetic acid.

Figure 16b is the flow sheet configuration after step 2. Regenerated wash liquid is used for the wash unit (W) (*Rule 9*). The liquid effluents from the wash unit and the dewatering step can be sent to the crystallizer to combine with fresh water for adjusting the acetic acid concentration in the crystallizer (*Rule 13*). The filtrate from the filter is sent to the solvent recovery system (*Rule 12*).

The complete flow sheet is shown in Figure 16c. There is only one feed stream to the solvent recovery system which is based on liquid–liquid extraction. There are three exit streams. Water is sent to the wash unit as regenerated wash liquid and to the crystallizer to adjust the acid concentration.

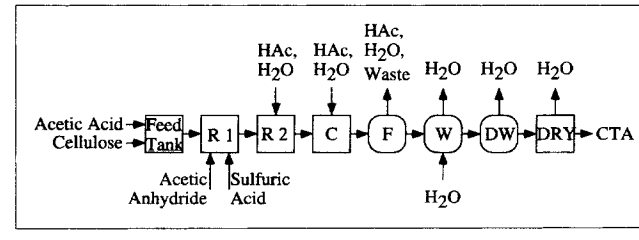

Figure 16a. Flow sheet configuration for cellulose triacetate process in Step 1.

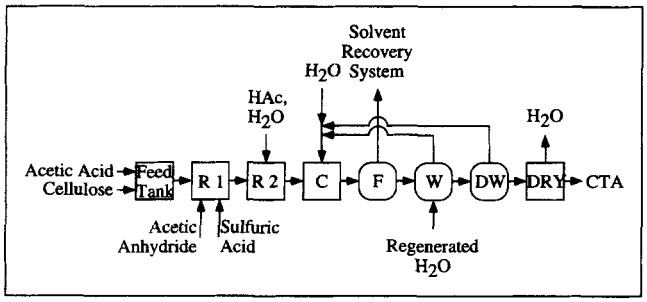

Figure 16b. Flow sheet configuration for cellulose triacetate process in Step 2.

Acetic acid is sent to the feed tank. An 80% acetic acid solution is sent to the saponification reactor (R2). The waste is purged.

Example 2: Itaconic acid process

Itaconic acid is an unsaturated dicarboxylic acid which can be produced by fermentation (Pfeifer et al., 1952). Solid wastes formed during fermentation have to be removed before sending the solution to the crystallizer to recover the product. The itaconic acid concentration in the fermentor effluent is quite dilute. The crystals obtained from the primary crystallizer are colored by an impurity. Water can be used as the wash liquid. Cooling crystallizers are used for both the crystallization and recrystallization steps.

Flow Sheet Generation. A complete flow sheet is shown in Figure 17. After the fermentation tank (FER), a filter (F1) is used to remove the solid waste from the slurry. A preconcentrator (CON) removes the excess solvent from the filtrate (*Rule 2*) before sending it to the primary crystallizer (C1). Filter F2 is used to recover the solids from the crystallizer effluent. To obtain a white crystalline product, decolorization of the crystals with carbon is accomplished with a recrystallization step (DS-F3-C2) (*Rule 3*). A wash unit (W1) for solvent switching before recrystallization is necessary (*Rule 4*). Another wash unit (W2) is used after filter F4 to wash off the occlusion impurity from the filter cake (*Rule 5*) before sending the cake to the dewatering step (DW) and dryer (DRY).

To complete the interconnections among these required units, rules in step 2 are used. Regenerated water is used for the last wash unit, W2 (*Rule 9*). The effluent streams from

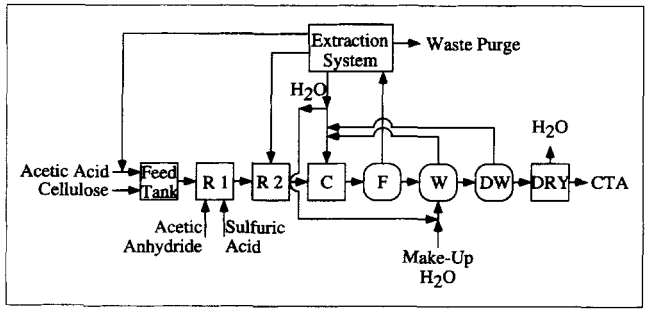

Figure 16c. Flow sheet configuration for cellulose triacetate process in step 3.

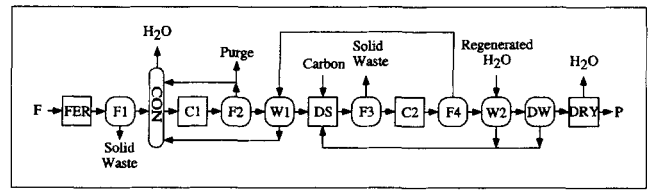

Figure 17. Flow sheet configuration for itaconic acid process.

W2 and the dewatering step (DW) are sent to the dissolution tank (DS) to be reused as the dissolution solvent (*Rule 10*). The filtrate from F4 is sent to the first wash unit as wash liquid since its impurity concentration is lower than that of the trapped liquid in the filter cake (*Rule 10*). The liquid effluent from W1 is then sent to the concentrator (CON) to recover the wash liquid (*Rule 12*). Part of the filtrate from the filter F2 is recycled back to the concentrator for complete recovery of itaconic acid (*Rule 14*). Note that although a cooling crystallizer is used here, the concentrator performs the same function as an evaporator crystallizer. The rest is purged to remove the impurity (*Rule 8*).

The procedure was applied to other case studies. For example, an evaporative crystallizer is used in a salt plant (Rossiter and Douglas, 1986). To completely recover the salt, the effluent mother liquor after filtration is recycled back to the crystallizer (*Rule 14*). A hydrocyclone/centrifuge combination serves as the filtration system (*Rule 20*). Another example is the production of aspirin (Stoesser and Surine, 1961). It is produced by acetylation of the phenolic hydroxy group of salicylic acid with acetic anhydride. Acetic acid is a reaction byproduct which also serves as the reaction solvent. To recover the acetic anhydride in the filter cake, the crystals are washed first with glacial acetic acid. This wash stream is recycled back to the reactor. Then the filter cake is washed with water to get rid of reaction solvent (*Rule 6*). In a potash plant (Rajagopal et al., 1988), the evaporative crystallizer effluent is recycled back to the dissolver to replenish dissolved potash (*Rule 15*). Seed crystals are recycled from the solid–liquid separation system to the crystallizer in an alumina plant (*Rule 16*) (Hill and Ng, 1997).

Conclusions

A systematic procedure is presented for synthesizing the processing system upstream and downstream of a crystallizer. In an evolutionary manner, the procedure guides the user through five levels to generate flow sheet alternatives of a crystallization processing system. Guidelines are provided to help the user to add more details to the flow sheet at each level. These guidelines are generic in nature and are not expected to be exhaustive. Companies tend to have in-house rules and proprietary technologies that are not captured in this article. However, the procedure is structured in such a way that the user can enter additional rules for use in a particular industrial sector or company.

The present study has a number of limitations. For example, we assume that the crystallizer design and choice of solvents are fixed. However, it is well appreciated that many problems in the downstream processing system (such as

washing problems and prohibitively long filtration time) can be dealt with more effectively by changing the conditions at the crystallizer. Not all processes have separate filters, washing tanks, and dryers. Single equipment units are available that can perform filtration, washing, dewatering, and drying without transferring the product from unit to unit. Actually, one can also perform crystallization and drying in one unit as in the prilling operation of a bisphenol A process. The choice of solvent has not been considered. In addition to its effect on reaction and crystallization, its surface tension can affect residual moisture content; its density can affect crystal settling velocity in a tank; and its volatility can affect the ease of solvent recovery. Also, energy issues related to crystallization processing systems have not been addressed. Relaxation of these limitations is under way.

While we believe the flow sheet configurations generated with the present procedure represent the best alternatives, a more rigorous mathematical scrutiny is needed to determine the globally optimal design. One alternative to the present heuristic-based approach is to formulate a mass-exchange network problem (El-Halwagi and Manousiouthakis, 1989, 1990) in which both thermodynamic limitations and flow sheet configurations are considered. Another is to tackle the synthesis task as an optimization problem (Grossmann and Daichendt, 1996). A superstructure which embeds all possible processing units and potential interconnections among them is first formulated. For a specified objective function, the optimal flow sheet is found within this superstructure by solving the corresponding mixed integer nonlinear programming problem. Figure 18 shows a possible general superstructure for a crystallization processing system where the wash liquid is the same as the recrystallization solvent. It is constructed by including some of the optional functions stipulated by rules 1 through 21 such as the use of a preconcentrator (CON) after the reactor, a hydrocyclone (HC) after the primary crystallizer (C1), countercurrent washing (W1-F2-W1'), and recrystallization (DS-F3-C2) in the superstructure. Then, bypass routes (dashed lines, 1 to 6) are added to allow an optimal flow sheet to skip these optional functions. Bypass route 6 represents the possibility that the wash solvent from W2 is more than the amount required for dissolution. The excess solvent is sent to W1' (*Rule 11*). If wash liquid is different from the recrystallization solvent, the wash liquid from W2 and DW is then sent to W1' as wash liquid. The filtrate from F4 is sent to the solvent recovery system to recover the recrystallization solvent for the dissolver, DS (dotted lines).

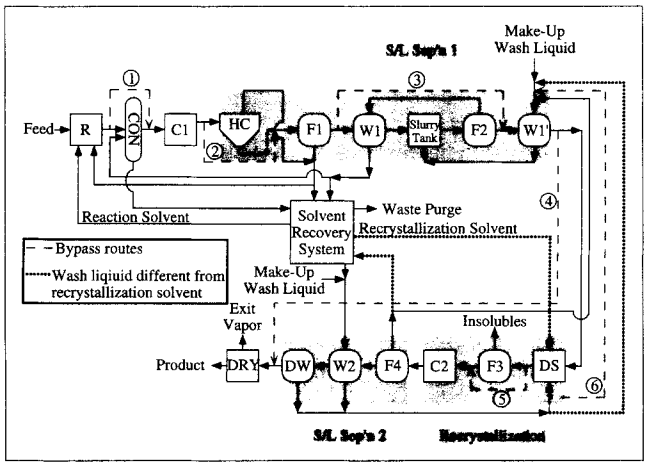

Figure 18. Superstructure of a crystallization processing system.

Acknowledgment

KMN would like to acknowledge the considerable influence on this article of the many stimulating discussions on crystallization system synthesis during his sabbatical leave at DuPont Central R&D. Financial support from the National Science Foundation (grant CTS-9211673) is gratefully acknowledged.

Notation

C_l = impurity level in the product, kg impurity/kg crystal of product
$C_l(i)$ = impurity concentration in stream i, kg solute/kg solvent
f_{DW} = fraction of liquid removed from the filter cake in dewatering
F = flow rate, kg/h
$F_m(i)$ = flow rate of component m in stream i, kg/h
N_j = wash ratio for the jth wash unit

Subscripts and superscripts

CCD = two-stage countercurrent washing with dewatering
T = total amount

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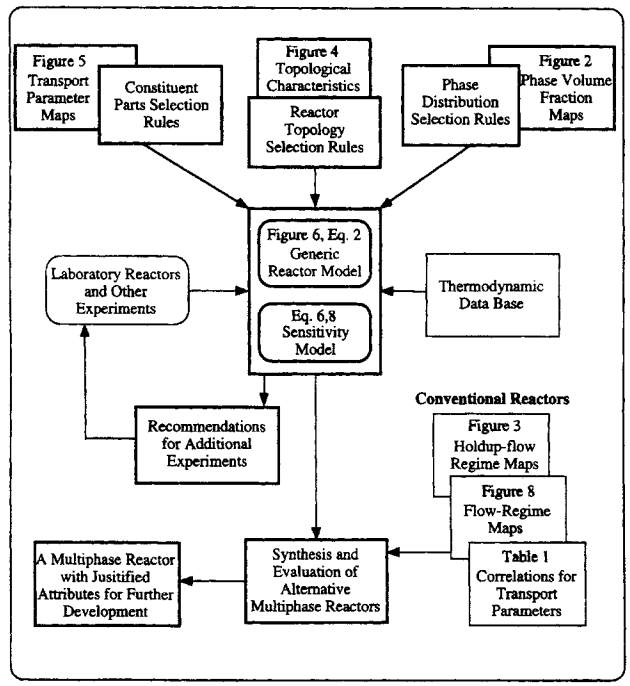
Corrections

In the article titled "Screening Procedure for Synthesizing Isothermal Multiphase Reactors" by Kelkar and Ng (July 1998), the following corrections are made:

Equation 19 on p. 1570 is corrected to

$$\phi = \frac{d_p}{6}\sqrt{\frac{k\rho_p}{D_l}} \qquad (19)$$

Correct Figure 7 on p. 1571 is



In Table 3 (p. 1574), the arrows (↓) were not included in the following six places: in iteration 1, between "0.086" and "3.76"; in iteration 2, between "1.53" and "0.168," between "0.14" and "0.71," and between "7.63" and "0.6"; in iteration 3, between "0.324" and "1.45"; and in iteration 4, between "0.19" and "30.3."

In Table 5 (p. 1577), the arrows (↓) were not shown in the following seven places; in iteration 1, between "0.003" and "0.0," between "1.57" and 4.995," and between "1.29" and "3.16"; in iteration 2, between "0.03" and "0.0," between "1.14" and "0.196," and between "4.42" and "0.122"; and in iteration 3, between "7.92" and "0.39."