

Environmentally Friendly Heterogeneous Azeotropic Distillation System Design: Integration of EBS Selection and IPS Recycling

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In chemical industries, waste solvents are considered to be the main source of pollution, whether it involves a batch process or a continuous process. Thus the separation of in-process solvents (IPS) from waste solvent streams, which is considered as *process design*, and the selection of environmentally benign solvent (EBS) to retrieve IPS, which is considered as *product design*, and are two important issues in waste solvents treatment problems. Because these two procedures could interact, it is necessary to integrate them into one framework based on the concern of cost, environmental quality, etc., to ensure better performance. In this work, we present an approach that utilizes three different methodologies at three different steps. In the process design step, the combination of residual curve maps (RCMs) analysis and P-graph technique are used to identify a separation superstructure. In the product design step, the computer-aided molecular design (CAMD) results obtained from previous work (Kim, K.-J.; Diwekar, U. M. *Ind. Eng. Chem. Res.* 2002, 41, 1285–1296) are used as replacements for conventional solvents such as ethyl acetate. A multi-objective optimization (MOP) framework under uncertainty, in which process design and product design are combined together and with solvents recovery rate, process operability, and environmental impacts like LC₅₀, LD₅₀ included in the objective function, is developed in the Aspen Plus simulator. The methodology is presented in the context of continuous separation of the acetic acid–water system. More Pareto optimal solutions have been identified in this work compared to the earlier work of Kim and Diwekar (*Ind. Eng. Chem. Res.* 2002, 41, 1285–1296).

1. Introduction

Due to increasing stringent regulations on environmental impact, environmentally benign chemicals need to be developed for the existing chemical processes. With the development of advanced chemicals with different physical and chemical properties, the corresponding optimal operation conditions and the process structures need to adapt to such changes. This new challenge makes it necessary to combine chemical synthesis and process synthesis together as an integrated structure that needs to be solved simultaneously to decrease environmental impact while keeping process performance competitive. Schug et al.¹ presented interval reasoning algorithms for this combination in a waste vitrification system. Hostrup et al.² formulated an MINLP problem for the design of environmentally benign processes. Eden et al.³ developed a property clustering approach that enables performing design on a component-free basis. In this paper, we will discuss an integrated product and process design of a heterogeneous azeotropic distillation system, in which acetic acid and water are separated by introducing an EBS. Acetic acid (HOAc), an IPS, is a valuable chemical but also a pollutant when released to the environment. HOAc can be directly separated from water in a single distillation column; however, because of the existence of tangent pinch close to pure water and the high boiling temperature of water and acetic acid (100 °C and 118 °C), it would be highly expensive to satisfy the purity requirement with direct distillation. Instead of using a

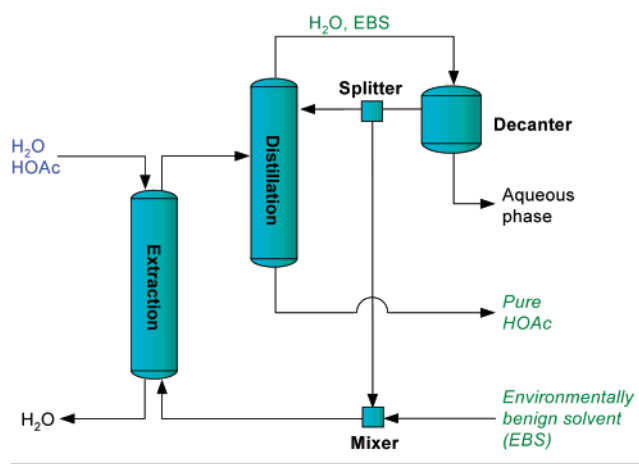


Figure 1. Conventional process of separating the water–acetic acid system (from Eastman Chemical Co.).

single distillation column, this separation, in practice, consists of adding another foreign agent to the water–HOAc system to form a minimum-boiling heterogeneous azeotrope. Adding this new foreign agent decreases the capital and operating cost, but the existence of the heterogeneous azeotrope increases the complexity and this leads to a choice of multiple process paths. The majority of available methods for selecting a possible process resort to a geometric method with graphical representation of azeotropes, residual curve maps (RCMs), and distillation boundaries. One such process employed in Eastman Chemical⁴ is depicted in Figure 1 which shows an example developed through heuristic strategy. The heuristic method is straightforward, but

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drawbacks are also obvious. It does not guarantee the identification of the best feasible structure; instead, the final process only depends on designer's personal experience. A graph theoretical approach, namely, the process graph (P-graph) based approach,⁵⁻⁸ can find all possible sets of structures from candidate operating units by which the desired products and necessary intermediate products leading to final products are produced. However, the "possible" here only means combinatorially possible. Further, P-graph analysis assumes a sharp split in the distillation column without considering reflux effect, which is an important factor in distillation operation. Therefore, considering P-graph alone is insufficient for identifying feasible and practical structures; further analysis facilitated with RCMs has also been done in this paper.

Product design is an approach to identify candidate EBS molecules that have desirable physical, chemical, and environmental properties. Computer-aided molecular design (CAMD)^{9,10} is one commonly used technique. CAMD, which works as the reverse use of group contribution methods, can automatically generate promising EBS molecules from their fundamental building blocks or groups. In this EBS selection step, former results from Kim and Diwekar,^{11,12} employing Hammersley stochastic annealing (HSTA)^{11,13} algorithm, are incorporated. The EBSs identified are (1) ethyl acetate, (2) propyl acetate, (3) isopropyl acetate, (4) methyl propyl ketone, (5) methyl isopropyl ketone, (6) diethyl ketone, and (7) methyl propionate.

The combination of IPS recycling and EBS selection poses a significant problem of a combinatorial explosion of process and chemical alternatives. In this paper, a MOP framework already developed by Kim and Diwekar is used.¹² The MOP framework will combine the newly formulated separation superstructure with product design, and the discrete optimizer is implemented in Aspen Plus as a user-supplied block instead of using it as a separate command structure as previously done. This implementation decreases the computation complexity of the MOP framework. The goals of this combination of EBS selection and IPS recycling are to achieve a high HOAc recovery yield, a high process flexibility, and low environmental impact (EI).

This paper has two main sections: the process synthesis, and coupled EBS selection, and IPS recycling as a MOP problem. The section of process design describes synthesis of the azeotropic-distillation system. The MOP problem section addresses the MOP framework and formulates a MOP problem, which is solved simultaneously for integrated EBS selection and IPS recycling.

2. Azeotropic-Distillation Process Design with the P-Graph

2.1. Material Partition. Residual curve maps (RCMs)¹⁴ contain important information (distillation boundary, azeotrope, etc.) of multicomponent mixtures. The mathematical model (eq 1) of RCMs is derived from the simple distillation, or open evaporation, of a mixture.

$$\frac{d\mathbf{x}}{d\xi} = \mathbf{x} - \mathbf{y} \quad (1)$$

where \mathbf{x} is the state vector of $(c - 1)$ independent liquid-phase mole fractions and \mathbf{y} the corresponding vector of equilibrium vapor phase mole fractions. ξ is a dimen-

sionless nonlinear transformation of the real time t . The synthesis and design of the azeotrope distillation system are generally based on heuristic methods which already have achieved some notable accomplishments. However, the issues regarding generation of feasible alternative flow sheets and construction of a superstructure linking all conceivable processing equipment systematically are far from resolved. To automate the synthesis and design process, the P-graph technique, which is based on the graph theory (Appendix A), is used to facilitate the design process. In the P-graph technique, the foremost step is to identify possible intermediate materials which represent various critical points, lines, regions, or spaces on RCMs. Since there is an infinite number of points on the residual curve maps (RCMs), it is impossible to analyze every point. To simplify this complexity, the area or space of RCMs is partitioned to represent the input and output of different operating units, the desired pure components, and feed streams. The partitioned materials are called lumped materials. There is no strict rule to govern the partitioning of RCMs. For a particular system, various strategies can be used depending on the extensiveness of the analysis to be conducted. Thus, a lumped material obtained from a simple partition can be further apportioned if a more detailed analysis is required. However, the following two rules must be obeyed here:

- (1) Different distillation regions must be labeled as different lumped materials.
- (2) A distillation region must be further partitioned if there are multiphase regions.

We use the same seven candidate solvents¹² for the acetic-acid and water system. These seven candidates have similar RCMs, azeotropes, and distillation boundaries. Therefore, only the water-acetic acid-ethyl acetate system is analyzed as an example. As can be seen in Figure 2, the water-acetic acid-ethyl acetate system is partitioned into 7 lumped materials, which are listed in Table 1. For example, the area (AWCB) is considered as one lumped material (L_2) because any mixture that lies in this region can be separated to pure acetic acid and the mixture of water/ethyl acetate by distillation. It is the same for other lumped materials; each mixture in a lumped material can be separated by the same technique. This system can also be further partitioned. For example, lumped material L_3 (WCBW) in Figure 2 can be further partitioned into L_{3A} (WCW) and L_{3B} (WCBW). This is because, though they are both in the same two-liquid-phase region, they are different when an extractor is used to obtain highly pure water that lies on point W. The material L_{3A} cannot be fed to the extractor because the raffinate of an extractor can only be on the curve CB. If we choose material L_{3A} as the feed, then the raffinate will be on the curve WC, which is not possible. In fact, this further partition is not necessary in this problem, the reason being the following: first, thermodynamic models are not accurate; second, the smaller region a lumped material is, the lower operability a process has; third, further partition will exponentially increase the number of solution structures, which will tremendously increase the complexity of the problem.

2.2. Identify Operating Units Producing Desired Final Products and Intermediate Materials. The operating units used in azeotropic distillation generally are distillation columns, mixers, decanters, and extractors. The feasible distillation here is considered to be a

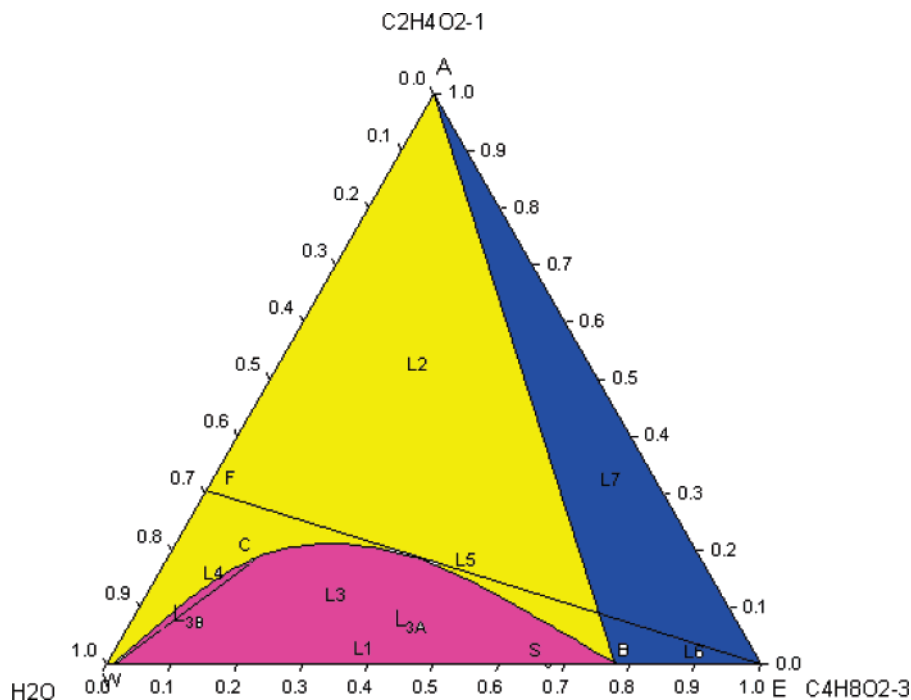


Figure 2. RCM of the water–HOAc–EtOAc system with lumped materials; S is azeotrope.

Table 1. Partition Materials of the Water–Acetic Acid–Ethyl Acetate System

index	partitioned materials	area	operating units ^a
1	F	F	FEED
2	A	A	S
3	W	W	EXT
4	L1	WB	S
5	L2	AWCBA	M
6	L3	WCBW	M
7	L4	WC	D
8	L5	CB	D
9	L6	BE	S
10	L7	ABE	M

^a S: distillation column; EXT: extractor; D: decanter; M: mixer.

sharp split, which means that the products lie only on the boundary of the distillation regions.

The desired products of this system are pure water (W) and HOAc (A). According to Figure 2, the potential operating units producing HOAc (A) are distillation columns, which take L₂, L₃, L₄, L₅, and L₇ as the feed and produce HOAc as the bottom product. The potential operating units producing water are decanters and extractors, which take L₁ or L₃ as feeds. Similarly, the operating units for generating intermediate materials leading to final products are identified until all the intermediate materials are generated by some operating units. All the operating units are listed in Table 2.

2.3. Generate and Classify Feasible Structures.

The complete set of feasible process structures is generated by the algorithm: Maximal structure generation (MSG).¹⁵ The maximal P-graph structure for this system is shown in Figure 3.

Further detailed thermodynamic analyses are carried out to eliminate some infeasible structures. The following rules are followed:

- (1) Structures with byproducts are eliminated.
- (2) Since there is only one distillation region of the water–acetic acid–ethyl acetate system, structures using more than one distillation column are eliminated.

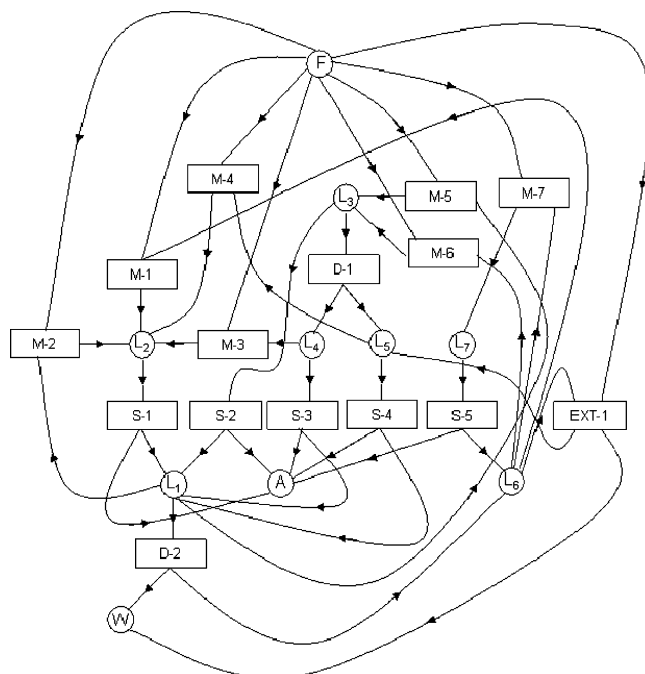


Figure 3. Maximal P-graph structure of the ethyl acetate–water–acetic acid system.

The defined byproducts of this system are the mixtures of three pure components such as L₄ and L₅ as shown in Figure 2. The main objective of this process is to separate acetic acid from water; hence, it would not be practical to use a process discharging the mixtures of acetic acid and water. Since the added solvent can also be redirected upstream as a recycle stream, then structures without reusing solvent are also eliminated. Thus, any structure with byproducts is considered incomplete.

The existence of a single distillation region and an azeotrope of water/ethyl acetate lead to the fact that no matter where the location of the feed composition is, the

Table 2. List of Operating Units

index	operating units	type
1	{L2},{L1,A}	distillation column(S-1)
2	{L3},{L1,A}	distillation column(S-2)
3	{L4},{L1,A}	distillation column(S-3)
4	{L5},{L1,A}	distillation column(S-4)
5	{L7},{L6,A}	distillation column(S-5)
6	{F,L6},{L5,W}	extractor(EXT-1)
7	{F,L6},{L2}	mixer(M-1)
8	{F,L1},{L2}	mixer(M-2)
9	{F,L4},{L2}	mixer(M-3)
10	{F,L5},{L2}	mixer(M-4)
11	{F,L1},{L3}	mixer(M-5)
12	{F,L6},{L3}	mixer(M-6)
13	{F,L6},{L7}	mixer(M-7)
14	{L3},{L4,L5}	decanter(D-1)
15	{L1},{L6,W}	decanter(D-2)

bottom product is the component with the highest boiling point, which is acetic acid in this case, and the top product is the azeotrope with the lowest boiling point. The redundant use of the distillation column would not produce any different product, but would definitely increase the capital and operating cost. So structures with more than one distillation column are also eliminated without further consideration.

After these eliminations, several feasible structures exist. These feasible structures can be classified into two categories, C_1 and C_2 . Category C_1 uses direct distillation that includes two structures and C_2 uses an extractor before distillation that includes eight structures.

Two structures in C_1 take the ternary mixture as the feed to the distillation column; the bottom product is pure acetic acid, while the distillate is the mixture of water and ethyl acetate, which lies in the two-phase region. Then this mixture is decanted, the organic phase is recycled, and the aqueous phase, which is highly pure water, is discharged for further treatment. The difference between these two structures is that, in one structure, the distillate of the azeo-column as well as the organic phase after decanting is recycled to mix with the feed to the distillation column. While in the other structure, only the organic phase of the decanter is recycled to mix with the feed stream as new feedstock.

Each of the structures in C_2 consists of an extraction column followed by a distillation column. The feed stream enters the extraction column, in which ethyl acetate extracts acetic acid from the water. The extract is then supplied to the distillation column where the bottom product is pure acetic acid and the top product is a heterogeneous mixture of water and ethyl acetate. Then this mixture is decanted. The differences between various structures in C_2 are the recycle streams to the distillation column, which can be either distillate from azeo-column, or organic phase from decanter, or nothing.

To operate a process described by C_1 , the mixture composition of water and acid acetate can lie on the entire line of AW (Figure 2). But if we operate a process described by C_2 , the feedstock composition can lie only on FW because the tangent line of the liquid-liquid envelope drawn from the pure ethyl acetate (E) intersects AW at F. Because the liquid-liquid envelope is thin, the operability of this process is low. But when feed composition lies on the line WF, the processes in C_2 are superior to the processes in C_1 considering the operating cost of the distillation column. This is because if the same amount of feedstock is treated, a large

portion of aqueous phase will be discharged from the extractor without going into the distillation column. This definitely can decrease the operating cost.

On the other hand, because of the sharp split assumption of the distillation column, the effect of the reflux stream is not considered, which will add another degree of freedom to the process. This is discussed below.

2.4. Effect of Reflux Stream. The top vapor composition of the distillation column, y_1 , is constant, reflecting the existence of the azeotrope. To obtain the pure acetic acid as the bottom product, the reflux composition, feed, distillate, bottom product, and reflux flow rate of the azeotropic distillation column have to be changed according to the fluctuation of the feedstock composition. The top product of the distillation column is the heterogeneous azeotrope of water and ethyl acetate, which can then be decanted to aqueous phase and organic phase. Therefore, there are four choices for the reflux stream given as follows: (1) the heterogeneous azeotrope, (2) the organic phase, (3) the aqueous phase, and (4) the mixtures of organic phase and aqueous phase.

Different selections will directly affect the operability of a process. Since the top vapor composition y_1 and the bottom product composition x_n are constant, the composition of the feed and reflux must stride across line SA (Figure 2) according to the lever rule. The choice of using heterogeneous azeotrope as the reflux makes this process hard to operate because the reflux composition r_1 coincides with y_1 , which decides that the feed composition can lie only on line SA. Otherwise, the bottom product will not be pure acetic acid.

If the organic phase is used as reflux, whose composition lies on point B, the feed composition must lie in the region ASW. Similarly, the third choice needs the feed composition to lie in the region ABS. These two choices have larger operating space than the first case, but the change of feed composition from one side to the other side can also deteriorate this process by producing nonpure acetic acid, which is either a mixture of water and acetic acid or a mixture of acetic acid and ethyl acetate.

The fourth choice uses the mixture of organic phase and aqueous phase as the reflux. The composition of this mixture lies on line WB; thus, feed composition can be on either side of line SA. This character gives the flexibility of the azeotrope distillation column feed composition. Considering the advantages of the fourth choice, the mixture of organic phase and aqueous phase is used as reflux stream in our case study.

2.5. Generation of Superstructure for MOP. The differences between different structures are recycle streams to the distillation column and the destination of the feedstock stream. This characteristic opens the possibility of combining all these structures together by adding splitters to each possible recycle stream and feed stream to form a superstructure of this separation system. The split fractions range from 0.0 to 1.0, which determine the distribution of streams between different operating units. First, a splitter is added after the feed stream. So the feed stream can go either to the extractor or to the distillation column. If the entire feed stream goes to the extractor, then it becomes the structure falling in the second category; otherwise, if the entire feed stream goes to the distillation column, then it becomes the structure belonging to the first category.

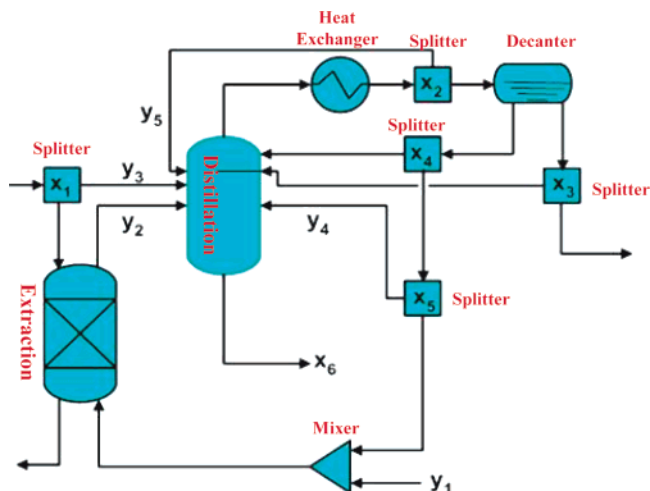


Figure 4. Superstructure of the water-acetic acid separation system.

The second splitter is added after heat exchanger, part of the distillate, goes to the decanter, while another part is recycled to the distillation column. When a splitter is added at each possible recycle stream, the superstructure is constructed as shown in Figure 4. The decision variables for this structure are $x_1, x_2, x_3, x_4, x_5, x_6, y_1, y_2, y_3, y_4,$ and y_5 . The optimal split fractions are determined in the third level of the MOP framework which is the continuous optimization loop (Figure 5 in the next section). The optimal feed locations, which are discrete variables, are determined in the fourth level of the MOP framework.

3. Integrated EBS Selection and IPS Recycling Problem: An MOP Problem

3.1. MOP Framework. The MOP framework is shown in Figure 5. The first level is a multiobjective optimization algorithm. The method used in this chapter is coupled simulated annealing and constraint method (SA-Constraint)¹¹ derived from MINSOOP algorithm¹⁶ for multiple objectives, in which one of the objectives is minimized while the remaining others are turned into inequality constraints with parametric right-hand-sides, L_k , which is shown as $L_2, L_3,$ and L_4 in eq 3. Solving repeatedly for different values of L_k leads to the Pareto set. The second level is discrete stochastic optimizer, which is a user-supplied block based on a simulated annealing algorithm. In this step all the solvent types, discrete decision variables, and number of random samples are determined. The third level is sampling in which Hammersley sequence sampling (HSS),¹⁷ which is at least 3–100 times faster than other current state-of-art techniques such as Latin hypercube sampling and Monte Carlo sampling, is used to propagate uncertain parameters. The fourth level is the formulation of the superstructure, which receives the process configurations from a discrete optimizer.

3.2. Problem Formulation. The objectives of this MOP problem under uncertainty are to maximize HOAc recovery (Z_1), minimize environmental impacts (EI) based on LC_{50} (Z_2) and LD_{50} (Z_3), and maximize the process flexibility (Z_4). Process flexibility in this paper is defined as the number of feasible solutions upon process uncertainty, which is expressed by feed variability. Because the flows of pollutants should be minimized and the solvents should be safe, the envi-

ronmental impact defined in terms of LC_{50} and LD_{50} is given below:

$$EI = \sum_i \text{streampollu} \sum_j \tan t \frac{\text{Flow}_{ij}}{LC_{50}(\text{or}LD_{50})} \quad (2)$$

The environmental impact based on fathead minnow LC_{50} (mg/L) represents aquatic ecotoxicity while the one based on oral rat LD_{50} (mg/kg) represents rodent toxicity (and possibly human toxicity).¹¹

$$\text{Min } Z_1 = -\text{HOAc in product}/\text{HOAc in feed} = f(x,y) \quad (3)$$

$$\text{s.t. } 1 \leq y_1 \leq 7$$

$$3 \leq y_2 \leq 10$$

$$1 \leq y_3 \leq 10$$

$$1 \leq y_4 \leq 10$$

$$1 \leq y_5 \leq 10$$

$$0.0 \leq x_1 \leq 1.0$$

$$0.0 \leq x_2 \leq 1.0$$

$$0.0 \leq x_3 \leq 1.0$$

$$0.0 \leq x_4 \leq 1.0$$

$$0.0 \leq x_5 \leq 1.0$$

$$20 \leq x_6 \leq 35$$

$$Z_2 = EI = \frac{\sum F_{\text{solvent,out}}}{\sum LC_{50,\text{solvent}}} + \frac{\sum F_{\text{HOAc,waste}}}{\sum LC_{50,\text{HOAc}}} \leq L_2$$

$$Z_3 = EI = \frac{\sum F_{\text{solvent,out}}}{\sum LD_{50,\text{solvent}}} + \frac{\sum F_{\text{HOAc,waste}}}{\sum LD_{50,\text{HOAc}}} \leq L_3$$

$$Z_4 = -\text{feasible runs}/\text{total runs} \leq L_4$$

$$y_i = \text{integer}$$

where x and y , which are also shown in Figure 4, are continuous and discrete decision variables. The continuous decision variable vector \mathbf{x} is [split fraction, distillation bottom rate]^T, and the discrete decision design vector \mathbf{y} is [solvent type, distillation feed locations, and recycle streams feed locations]^T. More decision variables are included due to the incorporation of the new superstructure compared to earlier MOP formulation.¹¹

3.3. Results and Discussions. The first step in solving MOP problems is to obtain a payoff table. A payoff table is widely used in decision analysis, where it specifies the alternatives, acts, or events. Especially in MOP, a payoff table shows a potential range of values of each objective. In more detail, a payoff table contains individual objective values (Z_k^*) for single optimization problems (k), and also provides potential ranges of the objectives on the Pareto surface (i.e., Z_L to Z_U). The minimum value (Z_L) of the objective is equal to the individual optimal value (Z_k^*), while the maximum

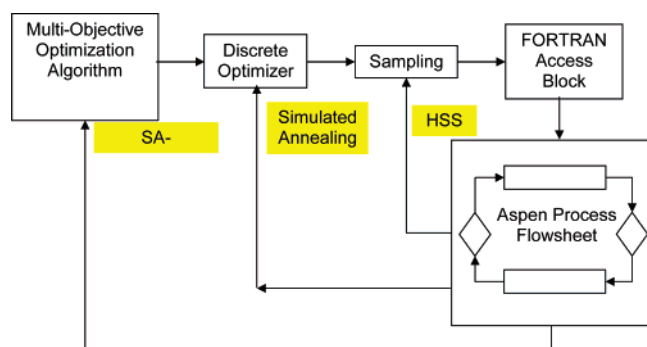
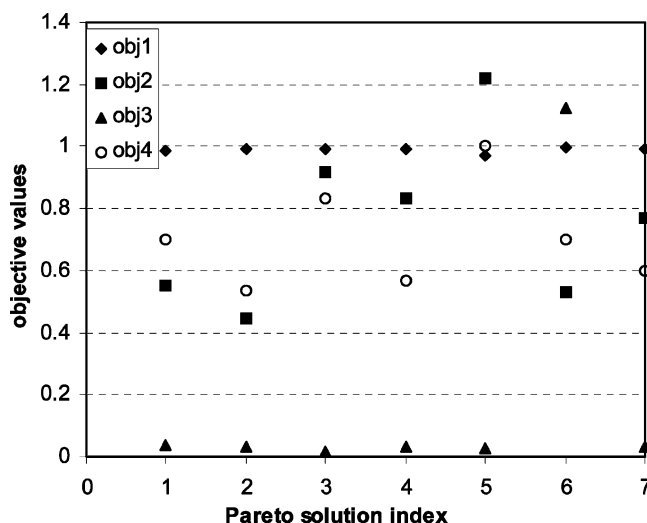
Table 3. Payoff Table at 5% Feed Flow Variation

k	objective	Z_L^*	Z_L	Z_U
1	HOAc recovery	0.9982		
2	EI based on LC ₅₀	0.4438	0.4438	1.2189
3	EI based on LD ₅₀	0.0161	0.0161	1.1262
4	flexibility	1.0000	1.0000	0.5333

Table 4. Pareto Solutions of the MOP Framework with 5% Feed Flow Variation (Normal Distribution)

index	y_1	y_2	y_3	y_4	y_5	recovery	EI(LC ₅₀)	EI(LD ₅₀)	flexibility
1	7	7	9	2	4	0.9842	0.5536	0.036	0.7
2	7	8	7	2	3	0.9908	0.4438	0.0328	0.5333
3	3	10	5	3	3	0.9891	0.9175	0.0161	0.8333
4	1	7	6	8	5	0.994	0.8315	0.0317	0.5667
5	3	8	2	5	1	0.9727	1.2189	0.0252	1
6	5	9	8	2	5	0.9982	0.5308	1.1262	0.7
7	1	10	4	10	3	0.9937	0.7714	0.0293	0.6

value (Z_U) of the objective is the maximum value of that objective found when minimizing the other objectives individually. In this way, an approximate range of the right-hand-side L_k in the Pareto surface is determined. Table 3 shows a payoff table for optimization under uncertainty, in which the variation in the feed flow rate is (-5% to +5%) of the nominal feed flow rate and is normally distributed. To clarify, the flow rate of each feed component is independently varied so that the total flow rate and its composition are altered. After the payoff table is found, SA-Constraint algorithm is used to generate the Pareto set. The solution of a multiobjective optimization problem is not a single solution but a complete nondominated or Pareto set, which includes the alternatives representing potential compromise solutions among the objectives. This makes a range of choice available to decision makers and provides them with the tradeoff information among the multiple objectives effectively. Totally, 7 Pareto optimal solutions are computed according to different solvent types, feed locations, and recycle schemes. They are shown in Table 4 and Figure 6. The solvent set includes ethyl acetate, isopropyl acetate, methyl isopropyl ketone, and methyl propionate. Methyl isopropyl ketone has the highest HOAc recovery ratio due to the high distribution coefficient; but it also has the highest EI which is due to the fact that EI is inversely proportional to LD₅₀ and the value of LD₅₀ in this case is the smallest (148 mg/kg) among all these seven solvents that ranges from 2000 mg/kg to 9000 mg/kg. Methyl propionate has the lowest EI (based on LC₅₀) because its LC₅₀ value (2240 mg/L) is the highest compared to methyl propyl ketone (1532 mg/L) and diethyl ketone (1540 mg/L). The main reason is low effluent of methyl propionate and for the same reason isopropyl acetate has the lowest EI (based on LD₅₀) value. Isopropyl acetate also possesses the

**Figure 5.** MOP framework for EBS selection and IPS recycling.**Figure 6.** Pareto set of superstructure.**Table 5. Pareto Solutions of Using the Conventional Process with 5% Feed Flow Variation (Normal Distribution)**

index	y_1	y_2	recovery	EI(LC ₅₀)	EI(LD ₅₀)	flexibility
1	3	6	0.9776	1.1447	0.025	0.7333
2	1	3	0.983	1.1283	0.0374	0.8
3	1	5	0.9869	0.9894	0.0337	0.5
4	7	5	0.9761	0.9078	0.0384	0.5333

highest flexibility. In the entire feed fluctuation range, it satisfies pre-requirements of HOAc recovery ratio, product purity. This high flexibility value ensures a large operating space, which is important when the feed composition change is very common. Ethyl acetate, the conventional solvent used to separate acetic acid from water, does not have any priority in any individual objective though it appears in two optimal solutions in the Pareto set. This proves that ethyl acetate has good average performance. When we compare Table 4 with Table 5, which represents the Pareto solutions using the conventional heuristic process¹¹ described in Figure 1, we can see that both these Pareto sets contain ethyl acetate, isopropyl acetate, and methyl propionate as optimal candidate solvents. But all the Pareto optimal solutions in Table 5 are dominated by Pareto optimal solutions in Table 4. From this comparison, we can see that new schemes produce better results than the conventional scheme.

4. Conclusions

In this paper, we introduced an integrated process and product design of a heterogeneous azeotropic distillation system. In the process design level, a superstructure is generated based on the P-graph. Further screening is carried out with the help of RCMs analysis. The new superstructure is then generated and incorporated into the MOP framework. Aspen Plus 11.1 is used to simulate the separation superstructure. The embedded NLP method in Aspen Plus is applied to choose the optimal operation conditions such as bottom flow rate of distillation column and split fractions. The user-supplied discrete optimizer based on simulated annealing is utilized to find the optimal solvent and optimal configurations of discrete decision variables such as solvent type and recycle feed point. This discrete stochastic optimizer block is incorporated as a user block in Aspen Plus, unlike the previously used strategy,¹¹

in which the discrete optimizer is implemented as a separate command, which decreases the computation complexity and interactions between Aspen Plus simulator and the external FORTRAN routine. The new scheme derived from the superstructure results in better and more Pareto solutions than the conventional heuristic scheme. This integrated MOP framework gives different solvent types and separation schemes considering different objectives. Methyl isopropyl ketone has the best value of the HOAc recovery ratio. Methyl propionate has the best EI value based on LC₅₀. Isopropyl acetate is superior to other solvents in objectives of EI based on LD₅₀ and flexibility.

Acknowledgment

The financial support of the EPA's STAR program through the grant #R38128 and NSF through the grant #CTS-0353088 are gratefully acknowledged. We greatly appreciate the help given by Dr. L. T. Fan in the P-graph formulation and also thank Dr. Ferenc Friedler for providing Process-Network Synthesis (PNSEditor) software.

Appendix: P-Graph Method

A process graph or P-graph in short is a unique bipartite graph representing the structure of a process system. In such a graph, the operating units are denoted by horizontal bars and their input and output materials by solid circles. A P-graph is a directed graph; the direction of the arcs is the direction of the material flows in the network; it is directed to an operating unit from its input materials and from the operating unit to its output materials. The P-graph illustrated in Figure 7a is the representation of the process shown in Figure 7b.

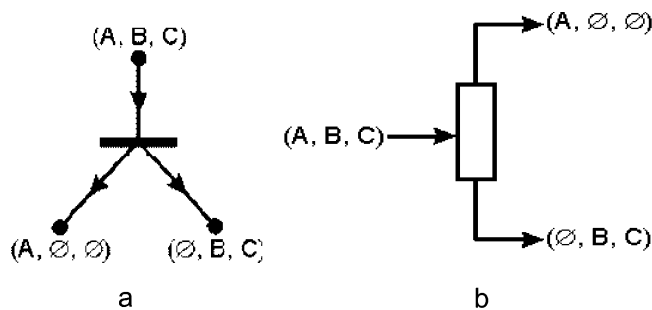


Figure 7. P-graph (a) representation of the block diagram (b).

In the P-graph technique, the final products and the operation units that produce such final products are identified first, and then the intermediate materials that can produce final products by identified operating units at previous steps are determined. This process is repeated until the complete P-graph of a process is constructed where all the input materials of the last step to the operating units are raw materials.

Nomenclature

LC₅₀ = lethal concentration at 50% mortality
 LD₅₀ = lethal dose at 50% mortality
 L_i = partitioned material, which represents input or output of operating units
 C_i = feasible structure category
 y₁ = top vapor composition of azeotropic-distillation column

x_n = bottom product composition of azeotropic-distillation column
 r₁ = reflux stream composition of azeotropic-distillation column
 x_{1,2,3,4,5} = split fraction
 x₆ = bottom flow rate of azeotropic-distillation column
 y₁ = solvent type
 y_{2,3,4,5} = location of feed tray
 Z₁ = acetic acid recovery
 Z₂ = environment impact based on LC₅₀
 Z₃ = environment impact based on LD₅₀
 Z₄ = process flexibility
 Z_L = lower bound of each objective
 Z_U = upper bound of each objective
 Z_k^{*} = optimal value of each objective

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Received for review June 17, 2004
 Revised manuscript received March 10, 2005
 Accepted April 4, 2005

IE049467Z