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

Weiyu Xu and Urmila M. Diwekar*
Center for Uncertain Systems, Tools for Optimization and Management (CUSTOM), Vishwamitra Research Institute, Westmont, Illinois 60559

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 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...
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 P-graph technique, 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) 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, employing Hammersley stochastic annealing (HSTA) 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, an MOP framework already developed by Kim and Diwekar is used. 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 azeotrope-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. Azeotrope-Distillation Process Design with the P-Graph

2.1. Material Partition. Residual curve maps (RCMs) 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.

\[
\frac{dx}{d\xi} = x - y
\]  

(1)

where \(x\) is the state vector of \((c - 1)\) independent liquid-phase mole fractions and \(y\) the corresponding vector of equilibrium vapor phase mole fractions. \(\xi\) is a dimensionless 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 solvents 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 \((L_3)\) 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 \(L_3\) in Figure 2 can be further partitioned into \(L_{3A}\) (WCW) and \(L_{3B}\) (WCB). 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 increases 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
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). 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.

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
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 would not produce any different product, but would decrease the operating cost. 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 strictly across line SA (Figure 2) according to the lever rule. The choice of using heterogeneous azeotrope as the reflux stream 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.
inequality constraints with parametric right-hand-sides, minimized while the remaining others are turned into for multiple objectives, in which one of the objectives is 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)\textsuperscript{11} derived from MINSOOP algorithm\textsuperscript{16} 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, $L_4$, which is shown as $L_2$, $L_3$, and $L_4$ in eq 3. Solving repeatedly for different values of $L_4$ 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),\textsuperscript{15} which is at least $3 \times 100$ 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 environmental impact defined in terms of LC$_{50}$ and LD$_{50}$ is given below:

$$EI = \sum_{i} \left( \sum_{j} \frac{Flow_{ij}}{LC_{50}(or LD_{50})} \right)$$

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).\textsuperscript{11}

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

s.t.  
$$1 \leq y_1 \leq 7$$
$$3 \leq y_2 \leq 10$$
$$1 \leq y_3 \leq 10$$
$$1 \leq y_4 \leq 10$$
$$1 \leq y_5 \leq 10$$
$$0.0 \leq x_1 \leq 1.0$$
$$0.0 \leq x_2 \leq 1.0$$
$$0.0 \leq x_3 \leq 1.0$$
$$0.0 \leq x_4 \leq 1.0$$
$$0.0 \leq x_5 \leq 1.0$$
$$20 \leq x_6 \leq 35$$

$$Z_2 = EI = \sum_{F_{solvent,out}} F_{solvent,out} / \sum_{LC_{50,solvent}} + \sum_{F_{HOAc,waste}} F_{HOAc,waste} / \sum_{LC_{50,HOAc}} \leq L_2$$

$$Z_3 = EI = \sum_{F_{solvent,out}} F_{solvent,out} / \sum_{LD_{50,solvent}} + \sum_{F_{HOAc,waste}} F_{HOAc,waste} / \sum_{LD_{50,HOAc}} \leq L_3$$

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

where $x$ and $y_i$, which are also shown in Figure 4, are continuous and discrete decision variables. The continuous decision variable vector $x$ is [split fraction, distillation bottom rate],

and the discrete decision design vector $y$ is [solvent type, distillation feed locations, and recycle streams feed locations]. More decision variables are included due to the incorporation of the new superstructure compared to earlier MOP formulation.\textsuperscript{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...
the fact that EI is inversely proportional to LD50 and sufficient; but it also has the highest EI which is due to the high distribution coefficient. Methyl isopropyl ketone has the highest HOAc recovery ratio due to the high distribution coefficient. Methyl propionate has the lowest EI (based on LC50) because its LC50 value (2240 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) value. Isopropyl acetate also possesses the same reason isopropyl acetate has the lowest EI (based on LC50) value.

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

Table 3. Payoff Table at 5% Feed Flow Variation

<table>
<thead>
<tr>
<th>k</th>
<th>objective</th>
<th>Z_L</th>
<th>Z_L</th>
<th>Z_U</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>HOAc recovery</td>
<td>0.9982</td>
<td>0.9982</td>
<td>1.2189</td>
</tr>
<tr>
<td>2</td>
<td>EI based on LC50</td>
<td>0.4438</td>
<td>0.4438</td>
<td>1.2189</td>
</tr>
<tr>
<td>3</td>
<td>EI based on LD50</td>
<td>0.0161</td>
<td>0.0161</td>
<td>1.2189</td>
</tr>
<tr>
<td>4</td>
<td>flexibility</td>
<td>1.0000</td>
<td>1.0000</td>
<td>0.5333</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>index</th>
<th>y_1</th>
<th>y_2</th>
<th>y_3</th>
<th>y_4</th>
<th>recovery</th>
<th>EI(LC50)</th>
<th>EI(LD50)</th>
<th>flexibility</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7</td>
<td>7</td>
<td>9</td>
<td>2</td>
<td>4</td>
<td>0.9842</td>
<td>0.5536</td>
<td>0.036</td>
</tr>
<tr>
<td>2</td>
<td>7</td>
<td>8</td>
<td>7</td>
<td>2</td>
<td>3</td>
<td>0.9908</td>
<td>0.4438</td>
<td>0.0328</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>10</td>
<td>5</td>
<td>3</td>
<td>3</td>
<td>0.9891</td>
<td>0.9175</td>
<td>0.0161</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>7</td>
<td>6</td>
<td>8</td>
<td>5</td>
<td>0.994</td>
<td>0.8315</td>
<td>0.0317</td>
</tr>
<tr>
<td>5</td>
<td>3</td>
<td>8</td>
<td>2</td>
<td>5</td>
<td>1</td>
<td>0.9727</td>
<td>1.2189</td>
<td>0.0252</td>
</tr>
<tr>
<td>6</td>
<td>5</td>
<td>9</td>
<td>8</td>
<td>2</td>
<td>5</td>
<td>0.9982</td>
<td>0.5308</td>
<td>1.1262</td>
</tr>
<tr>
<td>7</td>
<td>1</td>
<td>10</td>
<td>4</td>
<td>10</td>
<td>3</td>
<td>0.9937</td>
<td>0.7714</td>
<td>0.0293</td>
</tr>
</tbody>
</table>

Table 5. Pareto Solutions of Using the Conventional Process with 5% Feed Flow Variation (Normal Distribution)

<table>
<thead>
<tr>
<th>index</th>
<th>y_1</th>
<th>y_2</th>
<th>recovery</th>
<th>EI(LC50)</th>
<th>EI(LD50)</th>
<th>flexibility</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3</td>
<td>6</td>
<td>0.9776</td>
<td>1.1447</td>
<td>0.025</td>
<td>0.7333</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>3</td>
<td>0.983</td>
<td>1.1283</td>
<td>0.0374</td>
<td>0.8</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>5</td>
<td>0.9869</td>
<td>0.9894</td>
<td>0.0337</td>
<td>0.5</td>
</tr>
<tr>
<td>4</td>
<td>7</td>
<td>5</td>
<td>0.9761</td>
<td>0.9078</td>
<td>0.0384</td>
<td>0.5333</td>
</tr>
</tbody>
</table>

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

Figure 5. MOP framework for EBS selection and IPS recycling.
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

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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](Image)

**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
I1 = partitioned material, which represents input or output of operating units
C1 = feasible structure category
y1 = top vapor composition of azeotropic-distillation column
x1 = bottom product composition of azeotropic-distillation column
r1 = reflux stream composition of azeotropic-distillation column
x1,2,3,4,5 = split fraction
y6 = bottom flow rate of azeotropic-distillation column
y1 = solvent type
y2,3,4,5 = location of feed tray
Z1 = acetic acid recovery
Z2 = environment impact based on LC50
Z3 = environment impact based on LD50
Z4 = process flexibility
Z5 = lower bound of each objective
Zk* = optimal value of each objective

**Literature Cited**