Synthesis of Waste Interception and Allocation Networks

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This article introduces the novel concept of synthesizing waste-interception networks (WINs) and incorporates it within a mass-integration framework for the global allocation of pollutants. The essence of this notion is to provide selective interception and rerouting of undesirable species at the heart of the process instead of dealing with the pollutants in the terminal waste streams. It also provides a unified framework for simultaneously tackling gaseous and liquid pollution. Several tools are developed to track the pollutant throughout the process and determine the optimal interception policies. The problem is formulated as an optimization program that seeks to determine the optimum locations for intercepting the pollutants, extent of separation, and separating agents to carry out the interception tasks. Furthermore, the WINs can be used within a mass-integration scheme for the global allocation of species throughout the plant. These new concepts and associated mathematical formulation are demonstrated using a case study on the removal of a chlorinated hydrocarbon. This approach has benefits over conventional recycle/reuse (such as MEN synthesis).

Introduction

Pollution prevention is one of the most serious challenges currently facing the chemical process industry. In the United States alone, it is estimated that 12 billion tons (wet basis) of industrial waste are generated annually. To appreciate the proportions of the industrial-waste problem, it is interesting to note that the top 50 manufacturers of commodity chemicals generate about 0.3 billion ton per year which is 50% more than the total annual disposal rate for postconsumer municipal solid waste in the United States (Allen and Rosselot, 1994). The staggering magnitude of the industrial waste coupled with the growing awareness of the consequences of discharging effluents into natural resources have spurred several voluntary and legislated environmental measures. These corrective measures have prompted industry to seek various approaches to reduce any negative environmental impact.

In the 1970s, the main environmental activity of chemical processes was end-of-the-pipe treatment. This approach is based on installing pollution control units that can reduce the compositions of contaminants in waste streams to acceptable levels. Most of these units employ destructive techniques that convert the contaminants into more benign species (e.g., incineration, biotreatment, etc.). In the 1980s, the chemical process industries have shown a strong interest in implementing recycle/reuse policies in which pollutants are recovered from terminal streams (typically using separation processes) and reused or sold. This approach has gained significant momentum due to the realization that "waste streams and pollutants" may be valuable materials that can be recovered in a cost-effective manner. Since separation systems are essential in recycle/reuse policies, the past few years have witnessed a considerable progress in the area of designing separation networks for waste recovery. In particular, the powerful concepts of process integration and synthesis were developed to systematically accomplish the following:

1. Provide a global view of all waste streams in the plant (instead of tackling each waste stream independently).
2. Simultaneously screen all potential separation technologies that can be employed in recovering the pollutants.

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3. Identify performance targets (such as minimum cost of separating agents, maximum extent of mass integration) ahead of detailed design.

The area of systematically synthesizing optimal recycle/reuse networks for waste reduction was initiated by the introduction of the problem of synthesizing mass-exchange networks (MENs) (El-Halwagi and Manousiouthakis, 1989a,b). The design task of synthesizing a MEN is that of systematically identifying a cost-effective network of mass-exchange units that can selectively transfer certain undesirable species from a set of rich (waste) streams to a set of lean streams (mass-separating agents (MSAs)). The candidate MSAs to be screened are chosen based on commercial availability and physicochemical solvent-selection methods (e.g., Naser, 1995). A mass exchanger is any direct-contact mass-transfer unit operation that employs a MSA for the selective transfer of certain solutes. Examples of mass-exchange operations are stripping, solvent extraction, absorption, adsorption, leaching, and ion exchange. Several important categories of the MEN synthesis problem have been recently addressed. These include MENs with a single transferable pollutant (El-Halwagi and Manousiouthakis, 1989a, 1990a), multiple pollutants (El-Halwagi and Manousiouthakis, 1989b; Gupta and Manousiouthakis, 1994), regeneration of MSAs (El-Halwagi and Manousiouthakis, 1990b; Garrison et al., 1995), simultaneous waste reduction and energy integration (Srinivas and El-Halwagi, 1994a), chemically reactive separations (El-Halwagi and Srinivas, 1992; Srinivas and El-Halwagi, 1994b), fixed-load removal (Kiperstok and Sharratt, 1995), total cost minimization (Papalexandari et al., 1994), flexible performance (Papalexandari and Pistikopoulos, 1994; Zhu and El-Halwagi, 1994, 1995) and controllable MENs (Huang and Edgar, 1995; Huang and Fan, 1995). In addition, Wang and Smith (1994) addressed the case of MENs with a single lean stream (water) for wastewater minimization.

Systematic design techniques have also been devised for other separation systems that can be used in recycle/reuse networks. These efforts include the design of heat-induced separation networks (HISENs) in which the removal of the pollutants is accomplished via heating/cooling so as to affect a phase change (Dye et al., 1995; Richburg and El-Halwagi, 1995; El-Halwagi et al., 1994; Dunn et al., 1994) and pressure-driven membrane separations (Srinivas and El-Halwagi, 1993; El-Halwagi, 1992).

In addition to end-of-the-pipe treatment and recycle/reuse, pollution can be prevented by source reduction. Source reduction pertains to any step that limits the extent of waste generation at the sources. It focuses on in-plant activities that reduce the amount of hazardous substances entering any waste stream. Examples of source reduction include in-plant separation of hazardous species, process modifications, raw-materials substitution, and reaction-path changes. Source reduction extends the loop for environmental activities to include the plant itself along with the recycle/reuse and end-of-the-pipe treatment systems.

While much work has been done in the area of reducing the wastes by destroying/separating the pollutants from terminal streams using end-of-the-pipe treatment and recycle/reuse systems, very little work has been undertaken in the area of systematic design techniques for reducing pollution at the source. Jobak (1995) and Constantinou et al. (1995) developed material-substitution strategies to reduce pollution. Both works are based on group-contribution methods. Crabtree and El-Halwagi (1995) devised a systematic procedure to synthesize cost-effective environmental-acceptable reactions. Lakshmanan and Biegler (1995) developed reactor-network targeting strategies for waste minimization using multiobjective optimization.

As has been mentioned earlier, in addition to material substitution and reaction-system modification, in-plant separation and rerouting of pollutant-laden streams is an essential element in pollution prevention. It is based on intercepting and recycling some of the pollutant-laden streams so as to reduce the extent of pollution at the terminal waste streams. To date, there are no systematic procedures for the optimal design of in-plant material interception and rerouting for pollution prevention.

In this work, we introduce the new problem of synthesizing waste-interception networks (WINs). The proposed approach removes pollutants from in-plant streams instead of dealing with the pollutants in the terminal waste streams. It also provides a unified framework for simultaneously tackling gaseous and liquid pollution. Graphical representation tools are first developed to aid in tracking the pollutant throughout the process and to determine the optimal interception policies. The problem is formulated as a mixed-integer nonlinear program (MINLP) whose objective is to determine the optimum interception locations, extents, and separating agents throughout the plant. Furthermore, we discuss the role of interception as a key element of mass integration for pollution prevention. A case is solved and its intriguing results are discussed.

Problem Statement

The problem of synthesizing a waste-interception network WIN can be stated as follows. Given a process with terminal gaseous and liquid wastes that contain a certain pollutant, it is desired to identify a minimum-cost strategy for *in-plant* pollutant interception using mass-exchange operations that can reduce the pollutant load and concentration in the terminal waste streams to a specified level.

The WIN synthesis problem can be more formally stated as follows: given a process that disposes of a set $\boldsymbol{R}$ of terminal wastes containing a key undesirable species. These waste streams are classified into NR^{gas} gaseous wastes and NR^{liquid} liquid wastes such that $\boldsymbol{R} = \{i: i = 1, 2, \ldots, NR^{\text{gas}}, NR^{\text{gas}}+1, \ldots, NR^{\text{gas}} + NR^{\text{liquid}}\}$. The flow rate of each terminal gaseous waste, V_i^{Terminal}, and its discharge composition, y_i^{Terminal}, are given. Also, the flow rate of each terminal liquid waste, W_i^{Terminal}, and its discharge composition, z_i^{Terminal}, are given. It is desired to reduce the discharged amount of the undesirable species to a certain limit that complies with two types of environmental regulations:

1. The concentration of the pollutant in each terminal waste stream should be reduced to a target composition, $y_i^{\text{Terminal target}}$, for gaseous wastes and $z_i^{\text{Terminal target}}$ for liquid wastes, that is less than or equal to a regulated composition, $y_i^{\text{Terminal reg}}$ for gaseous wastes and $z_i^{\text{Terminal reg}}$ for liquid wastes, that is,

$$y_i^{\text{Terminal target}} \le y_i^{\text{Terminal reg}} \qquad i = 1, 2, \ldots, NR^{\text{gas}} \quad (1)$$

and

$$z_i^{\text{Terminal target}} \le z_i^{\text{Terminal reg}} \qquad i = NR^{\text{gas}} + 1, NR^{\text{gas}} + 2, \ldots, NR^{\text{gas}} + NR^{\text{liquid}}. \quad (2)$$

2. The total reduction in disposal load should be at least a fraction, α^{gas} for gaseous wastes and α^{liquid} for liquid wastes, of the original discharged load, that is,

$$\sum_{i=1}^{NR^{\text{gas}}} V_i^{\text{Terminal}} y_i^{\text{Terminal target}} \le (1 - \alpha^{\text{gas}}) \sum_{i=1}^{NR^{\text{gas}}} V_i^{\text{Terminal}} y_i^{\text{Terminal}} \quad (3)$$

and

$$\sum_{i=NR^{\text{gas}}+1}^{NR^{\text{gas}}+NR^{\text{liquid}}} W_i^{\text{Terminal}} z_i^{\text{Terminal target}} \le (1 - \alpha^{\text{liquid}}) \sum_{i=NR^{\text{gas}}+1}^{NR^{\text{gas}}+NR^{\text{liquid}}} W_i^{\text{Terminal}} z_i^{\text{Terminal}}. \quad (4)$$

The waste-reduction duty is to be accomplished by employing mass-exchange operations to intercept the pollutant inside the plant and/or at the terminal streams.

Throughout the plant, several gaseous and liquid streams contain the undesirable species. These streams are referred to as sources. The sources are composed of a gaseous set **GAS_SOURCES** = $\{v{:}v = 1, NV\}$ and a liquid set **LIQUID_SOURCES** = $\{w{:}w = 1, NW\}$. These streams are processed through a set **UNITS** = $\{u{:}u = 1, NUNITS\}$ of process equipment that is a subset of the total flow sheet. Two sets of candidate MSAs can be utilized to selectively intercept and remove the undesirable species. The set $SV = \{j{:}j = 1, 2, \ldots, NSV\}$ can be employed to remove the pollutant from gaseous sources and the set $SW = \{j{:}j = 1, 2, \ldots, NSW\}$ can be used to remove the pollutant from liquid sources. The supply and target compositions of each MSA (x_j^s, x_j^t for $j \in SV$ and X_j^s, X_j^t for $j \in SW$) are given. The flow rate of each MSA (l_j for $j \in SV$ and L_j for $j \in SW$) is unknown and is to be determined as part of the problem optimization. Figure 1 shows a representation of the WIN synthesis problem.

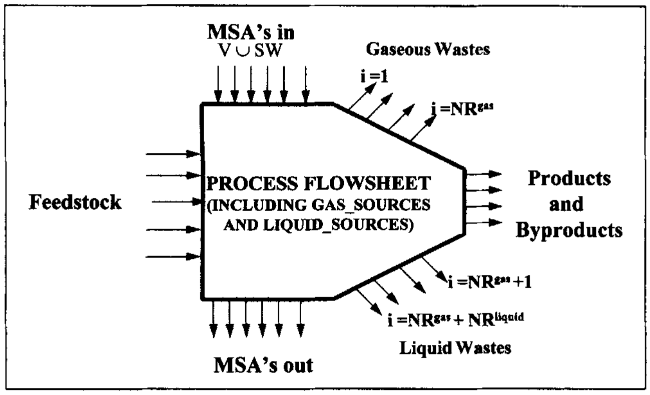

Figure 1. WIN synthesis problem.

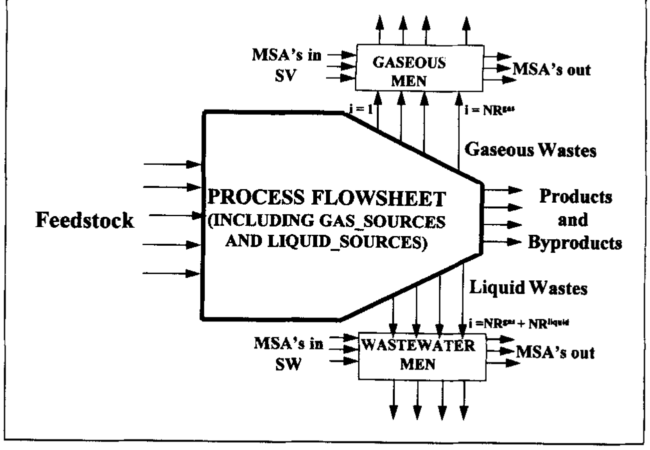

Figure 2. MEN synthesis problem for terminal streams.

It is beneficial to compare the WIN synthesis problem with the MEN synthesis task. As shown by Figure 2, the MEN synthesis is concerned with the separation of the pollutant from terminal streams only. Furthermore, gaseous pollution is tackled independently from liquid pollution. Since the terminal waste streams are included in the sets **GAS_SOURCES** and **LIQUID_SOURCES** (along with the in-plant streams), the WIN synthesis problem embeds the MEN synthesis task.

Design Approach and Challenges

Owing to the strong interaction among the various gaseous and liquid sources, the proposed WIN synthesis approach will be based on a fundamental understanding of the global flow of mass throughout the process so as to describe the propagation of the pollutant throughout the process. The term *interception* will be used to refer to the usage of a mass-exchange operation to selectively remove the pollutant from a pollutant-laden stream. The task of synthesizing an optimal WIN calls for addressing the following questions:

- Which phase(s) (gaseous, liquid) should be intercepted?
- Which process streams should be intercepted?
- To what extent should the pollutant be removed from each process stream?
- Which mass-exchange operations should be used for interception?
- Which MSAs should be selected for interception?
- What is the optimal flow rate of each MSA?
- How should these MSAs be matched with the pollutant-laden streams (i.e., stream parings)?

The aforementioned questions are highly combinatorial in nature and, in general, cannot be answered by simply enumerating candidate scenarios. Instead, a systematic approach is needed to generate the optimal solution. This approach is presented in the ensuing sections.

Solution Strategy

As has been mentioned earlier, the proposed solution approach is based on using fundamentals to capture the global insights for the pollutant flow throughout the process. In this context, a two-stage targeting approach will be adopted. In the first stage, the minimum operating cost of the interception network is determined without commitment to the network structure. Next, a network is synthesized so as to minimize the fixed cost that realizes the identified minimum operating cost. The total annualized cost is minimized by iteratively trading off the fixed and the operating costs using the minimum allowable composition differences (El-Halwagi and Manousiouthakis, 1990a).

Several tools will be developed to provide a global understanding for the flow of pollutants. In this context, a particularly useful tool is the "path-diagram" that we introduce in the next section.

Path diagram

The path diagram is a representation tool that captures the overall flow of the pollutant throughout the plant. It also relates the flow of the pollutant to the performance of the different processing units. A path diagram represents the load of the targeted species throughout the process as a function of its composition in carrying streams. Instead of considering the whole flow sheet, one should only keep track of the units involving the targeted species. To derive the mathematical expression for the path diagram, the pollutant is tracked throughout the process via material balances and unit-modeling equations.

In general, at least two path diagrams are needed; one for the gaseous sources and the other for liquid sources. On the gaseous path, each pollutant-laden gaseous stream (gaseous source) is represented by a node on a mass-composition diagram. These nodes are connected with composition profiles of the streams within the units. Since this article focuses on manipulating streams and not units, the exact shape of the composition profile within a unit is typically not needed. Therefore, these profiles can be approximated by piecewise-linear representation. Since mass flow is associated with a direction (from input of a unit to output of a unit), the path diagram is a directed graph (or digraph) in which the piecewise-linear profiles are treated as arrows. The directionality of these arrow reflects the orientation of mass flow with arrows tails emanating from inputs to units and arrowheads pointing toward output of units. Since a unit may have multiple inputs and outputs, each node may be associated with multiple arrowheads and tails. Once the gaseous path is developed, the same procedure is also followed in constructing the liquid-path diagram.

In order to demonstrate the construction of the path diagram, consider Figure 3, which illustrates a section of a process that involves the pollutant-laden streams. Figure 3 also shows the various loads and compositions of the pollutant throughout the process. For a given pollutant-laden gaseous stream, v, V_v is the flow rate of the stream, y_v is the composition of the pollutant, and Φ_v is the load of the pollutant in the stream defined as

$$\Phi_v = V_v y_v \qquad v = 1, 2, \ldots, NV. \tag{5}$$

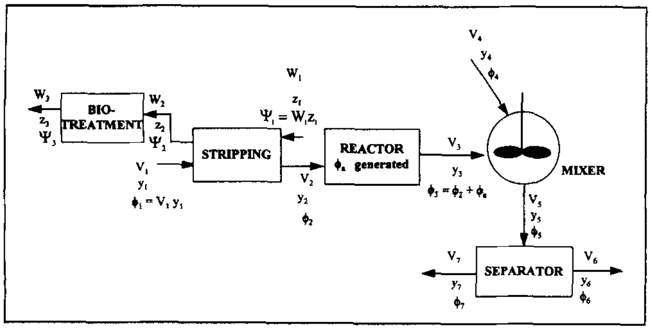

Figure 3. Units involving the pollutant in a generic process.

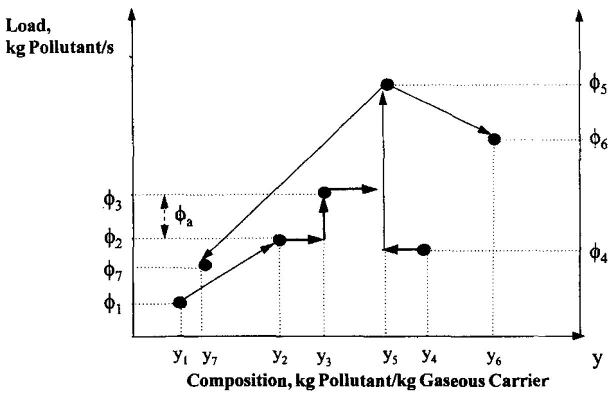

Figure 4. Gaseous path diagram for the pollutant.

Similarly, on the liquid path the load of the pollutant in the wth liquid source is given by

$$\Psi_w = W_w z_w \qquad w = 1, 2, \ldots, NW. \tag{6}$$

The path gaseous diagram for this process is given by Figure 4. The first step in Figure 3 is a stripping process in which the pollutant is transferred from a liquid stream (source $w = 1$) to a gaseous stream (source $v = 1$). Due to the countercurrent contact of the two streams, the path profile for each stream ($\Psi_w = W_w z_w$ and Φ_v vs. y_v) is given by a linear arrow extending between inlet and outlet compositions and having a slope equal to the flow rate of the stream. The gaseous stream leaving the stripper is then processed in a continuous stirred tank reactor where some additional mass of the pollutant, Φ_a, is generated. Owing to the complete mixing in the reactor, the concentration of the pollutant instantaneously changes from the inlet concentration, y_2, to the outlet concentration, y_3. Furthermore, the pollutant loading increases to $\Phi_3 = \Phi_2 + \Phi_a$. The effluent from the reactor is mixed with another process stream ($v = 4$) to give a resulting composition, y_5, and mass loading, Φ_5. The composition y_5 can be graphically determined using the lever-arm principle. The final operation involves the separation of the mixed stream into two terminal streams ($y = 6$ and 7).

Similarly, one can develop the liquid-path diagram as shown in Figure 5. It involves three nodes, $w = 1$–3, which are related by the stripper and the biotreatment units.

Since each node on the path diagram corresponds to a pollutant-laden stream (a source), the gaseous-path diagram has NV nodes, while the liquid-path diagram has NW nodes. Each node is related to the other nodes via process models (e.g., material balance, unit performance equations, etc.). For instance, let us consider a unit, u, which involves the pollu-

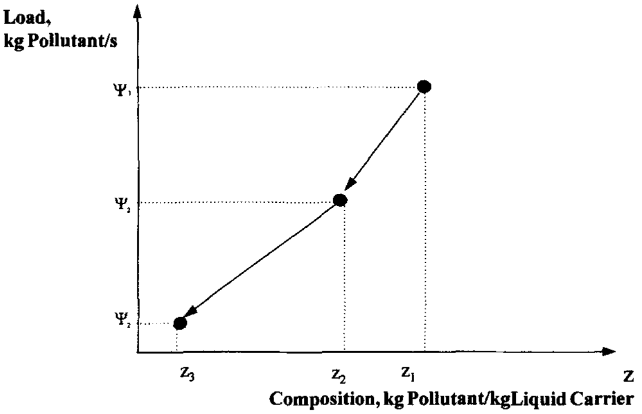

Figure 5. Liquid path diagram for the pollutant.

tant (i.e., $u \in$ **UNITS**). The gaseous and liquid streams that are inputs to this unit are described by the following two sets:

$\mathbf{GAS\_INPUTS}_u = \{v{:}v$ is a gaseous input stream to unit $u\}$

and

$\mathbf{LIQUID\_INPUTS}_u = \{w{:}w$ is a liquid input stream to unit $u\}$.

Also, the gaseous and liquid outputs from this unit are referred to as the following set of nodes

$\mathbf{GAS\_OUTPUTS}_u = \{v{:}v$ is a gaseous output stream from unit $u\}$

and

$\mathbf{LIQUID\_OUTPUTS}_u = \{w{:}w$ is a liquid output stream from unit$\}$.

Hence, the path diagram can be mathematically described as a function of the input and output nodes via the following equations.

Total Material Balances:

$$\sum_{v \in \mathrm{GAS\_OUTPUTS}_u} V_v + \sum_{w \in \mathrm{LIQUID\_OUTPUTS}_u} W_w = \sum_{v \in \mathrm{GAS\_INPUTS}_u} V_v + \sum_{w \in \mathrm{LIQUID\_INPUTS}_u} W_w \qquad u \in \mathbf{UNITS}. \quad (7)$$

If unit u involves streams that are not laden with the pollutant (i.e., neither gaseous nor liquid sources), they should be included in the material balance.

Pollutant Material Balance:

$$\sum_{v \in \mathrm{GAS\_OUTPUTS}_u} V_v y_v + \sum_{w \in \mathrm{LIQUID\_OUTPUTS}_u} W_w z_w + \mathrm{Net}_u = \sum_{v \in \mathrm{GAS\_INPUTS}_u} V_v y_v + \sum_{w \in \mathrm{LIQUID\_INPUTS}_u} W_w z_w \qquad u \in \mathbf{UNITS} \quad (8)$$

where the term Net_u accounts for the net loss of the pollutant within unit u (e.g., losses in fugitive emissions + depletion by chemical reaction − generation by chemical reaction, etc.).

Unit Modeling Equation(s):

$$(\Phi_v, y_v, \Psi_w, z_w{:}v \in \mathrm{GAS\_OUTPUTS}_u \text{ and } w \in \mathrm{LIQUID\_OUTPUTS}_u) = f_u(\Phi_v, y_v, \Psi_w, z_w{:}v \in \mathrm{GAS\_INPUTS}_u \text{ and } w \in \mathrm{LIQUID\_INPUTS}_u) \qquad u \in \mathbf{UNITS}, \quad (9)$$

where f_u is a vector of several performance equations relating outputs to inputs for unit u.

Equations 5–9 provide the proper degrees of freedom for constructing the path diagrams graphically and analytically. It is worth pointing out that the path diagram provides the big picture for mass flow. This is a fundamentally different vision from the equipment-oriented description of a process (the flow sheet), in which the big picture is lost. The path diagram can also be used to determine the effect of manipulating any node on the rest of the diagram. In addition, as will be shown later, it provides a systematic way for identifying where to remove the pollutants and to what extent they should be removed.

Effect of Interception on the Path Diagram

As has been mentioned before, the path diagram can be used to predict the effect of intercepting one stream on the rest of the streams. In order to quantify this relationship, let us consider that all gaseous and liquid nodes on the path diagrams are intercepted. Upon interception, the composition and load of the vth gaseous node are altered from y_v and Φ_v to y_v^{int} and Φ_v^{int}. Similarly, the composition and load of the wth liquid node are altered from z_w and Ψ_w to z_w^{int} and Ψ_w^{int}. For unit u, the output compositions and loads are now functions of the intercepted loads and compositions of the input streams. Therefore, Eqs. 8 and 9 become

$$\sum_{v \in \mathrm{GAS\_OUTPUTS}_u} V_v y_v + \sum_{w \in \mathrm{LIQUID\_OUTPUTS}_u} W_w z_w + \mathrm{Net}_u = \sum_{v \in \mathrm{GAS\_INPUTS}} V_v y_v^{\mathrm{int}} + \sum_{w \in \mathrm{LIQUID\_INPUTS}_u} W_w z_w^{\mathrm{int}} \qquad u \in \mathbf{UNIT} \quad (10)$$

and

$$(\Phi_v, y_v, \Psi_w, z_w{:}v \in \mathrm{GAS\_OUTPUTS}_u \text{ and } w \in \mathrm{LIQUID\_OUTPUTS}_u) = f_u(\Phi_v^{\mathrm{int}}, y_v^{\mathrm{int}}, \Psi_w^{\mathrm{int}}, z_w^{\mathrm{int}}{:}v \in \mathrm{GAS\_INPUTS}_u \text{ and } w \in \mathrm{LIQUID\_INPUTS}_u) \qquad u \in \mathbf{UNITS}. \quad (11)$$

Having identified the relationship between interception and the path diagrams, we next integrate the path and the mass-exchange pinch diagrams.

Integration of Path and Pinch Diagrams

A particularly useful tool in synthesizing MENs is the pinch diagram (El-Halwagi and Manousiouthakis, 1989a, 1990b). The essence of this tool is to construct a composite waste stream of all waste streams and a composite lean stream of all candidate MSAs to minimize the cost of MSAs. To demonstrate this tool, let us consider a mass exchanger for which the equilibrium relation governing the transfer of a key pollutant [for the case of multiple pollutants, the problem can be first solved for each pollutant independently. If the solution associated with one pollutant realizes the targets for the other pollutants, the problem is referred to as MEN with compatible targets (El-Halwagi and Manousiouthakis, 1989a); if the targets are incompatible, a more involved mathematical formulation should be used (El-Halwagi and Manousiouthakis, 1989b; Gupta and Manousiouthakis, 1994] from the vth waste stream to the jth MSA is given by the following isothermal linear [the cases of nonisothermal mass exchange and nonlinear equilibrium have been addressed by Srinivas and El-Halwagi (1994a,b)] expression

$$y_v = m_j x_j^* + b_j. \tag{12}$$

By employing a minimum allowable composition difference of ϵ_j, between the equilibrium and the operating lines, we get

$$y_v = m_j(x_j + \epsilon_j) + b_j \tag{13}$$

which can be used to establish a one-to-one correspondence among all composition scales for which mass exchange is feasible. The vector of ϵ_j's is an optimization variable. It is used to trade off fixed versus operating costs to minimize the total annualized cost (El-Halwagi and Manousiouthakis, 1990a). Next, each rich (pollutant-laden) stream is represented as an arrow whose tail corresponds to its supply composition and its head corresponds to its target composition with a slope equal to the stream flow rate. The waste streams are added using superposition to yield a rich composite stream. Similarly, a lean composite stream is generated by plotting the MSA's versus their composition scales. Optimization is used to determine the flow rates (slopes) of the lean streams so as to minimize the cost of MSA's while maintaining the lean composite stream completely above the rich composite stream to insure thermodynamic feasibility.

In conventional MENs, the supply and target compositions of all waste streams are determined *a priori*. However, in the case of WINs, the supply and target compositions of the rich streams to be intercepted are unknown. Indeed, the determination of these compositions is part of the solution and is strongly linked to the path diagram.

The relationship between the path and the pinch diagrams can be envisioned as shown by Figure 6, which illustrates the back-and-forth passage of streams between the two diagrams. Consider the gaseous nodes ($v = 1, 2, \ldots, NV$) that are passed from the path diagram to the pinch diagram. Upon interception, these streams change composition from y_v to the intercepted compositions y_v^{int} where $v = 1, 2, \ldots, NV$. Each intercepted stream is returned to the path diagram. According to Eqs. 10 and 11, this interception propagates throughout the whole path diagram affecting the other nodes. In turn, this propagation in the path diagram affects the pinch diagram by changing the rich composite stream. Consequently, the lean composite stream is adjusted to respond to the changes in the waste composite stream.

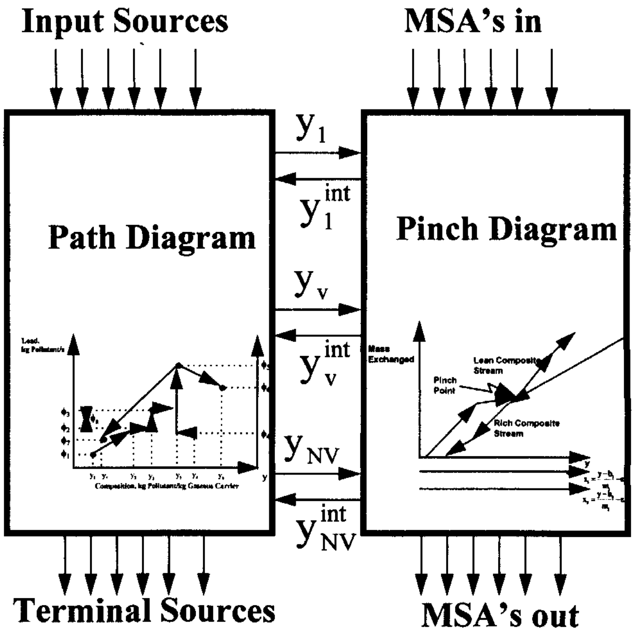

Figure 6. Integration of path and pinch diagrams.

In order to minimize the cost of MSAs using the pinch diagram, it is necessary to parametrize the rich composite stream as a function of path-diagram compositions. This task can be accomplished by extending the mixed-integer nonlinear representation proposed by El-Halwagi and Manousiouthakis (1990b) for regenerable MSAs to the situation of varying inlet and outlet compositions of rich streams. First, overall pollutant balance has to be satisfied for the gaseous sources. Hence,

$$\sum_{v=1}^{NV} V_v(y_v - y_v^{\text{int}}) = \sum_{j=1}^{NSV} l_j\left(x_j^t - x_j^s\right). \tag{14}$$

Next, a set P^{gas} of potential pinch points is defined to include all inlet compositions of rich and lean streams. (Pinch points are located at inlet of streams for the cases of linear and convex equilibrium functions. For the cases of nonconvex equilibrium, the pinch may lie at any operating composition (Srinivas and El-Halwagi, 1994b).) Below each potential pinch point, one can show (El-Halwagi and Manousiouthakis, 1990b) that:

$$\text{Mass lost by the rich streams} - \text{mass gained by the lean streams} \le 0 \tag{15}$$

with the equality applying at the true pinch point. Equation 14 can be mathematically described by

$$\sum_{v=1}^{NV} V_v\left[\lambda_{v,p}^{\text{int}}(y^p - y_v^{\text{int}}) - \lambda_{v,p}(y^p - y_v)\right]$$

$$-\sum_{j=1}^{NSV} l_j\left[\eta_{j,p}^s\left(x_j^t - x_j^s\right) - \eta_{j,p}^t\left(x_j^p - x_j^t\right)\right] \leq 0$$

$$\forall p \in \boldsymbol{P}^{\text{gas}}. \quad (16)$$

The binary coefficients $\lambda_{v,p}^{\text{int}}$, $\lambda_{v,p}$, $\eta_{j,p}^s$, and $\eta_{j,p}^t$ are defined in Appendix A.

Similarly, for interception of liquid streams, one can write the following pollutant balances:

Overall Material Balance:

$$\sum_{w=1}^{NW} W_w(z_w - z_w^{\text{int}}) = \sum_{j=1}^{NSW} L_j\left(X_j^t - X_j^s\right). \quad (17)$$

Material Balance below Potential Pinch Points:

$$\sum_{w=1}^{NW} W_w\left[\gamma_{w,q}^{\text{int}}(z^q - z_w^{\text{int}}) - \gamma_{w,q}(z^q - z_w)\right]$$

$$-\sum_{j=1}^{NSW} L_j\left[\beta_{j,q}^s\left(X_j^t - X_j^s\right) - \beta_{j,q}^t\left(X_j^q - X_j^t\right)\right] \leq 0$$

$$\forall q \in \boldsymbol{P}^{\text{liquid}}, \quad (18)$$

where the binary coefficients $\gamma_{w,q}^{\text{int}}$, $\gamma_{w,q}$, $\beta_{j,q}^s$ and $\beta_{j,q}^t$ are as defined in Appendix A.

Mathematical Formulation

Based on the foregoing discussion, we can now formulate the WIN synthesis task as an optimization program. A two-stage targeting approach is adopted. In the first stage, the minimum operating cost of the network is identified. Once a minimum operating cost is obtained, a WIN can be synthesized using MILP techniques and the fixed cost of the network can be traded off vs. its operating cost using the minimum allowable composition differences so as to minimize the total annualized cost of the system (El-Halwagi and Manousiouthakis, 1990a).

The mathematical formulation for WIN synthesis is given in Appendix B. This formulation is a mixed-integer nonlinear program (MINLP) that can be solved to determine the optimal flow rates of all MSAs, which streams should be intercepted, and the extent to which each stream is intercepted.

Graphical Generation of Initial Solutions

Due to the nonconvexity of the foregoing MINLP formulation, commercially available optimization software cannot guarantee the global solution of the problem. Therefore, it is beneficial to use graphical techniques to eliminate nonoptimal regions from the search space, determine near-optimal solutions, reduce problem dimensionality, and provide insights into the problem. A particularly useful concept stems from the previously discussed integration of path and pinch diagrams. After plotting the path diagram for the sources, corresponding composition scales for the MSAs are plotted using Eq. 13. Each MSA is then represented vs. its composition scale as a horizontal arrow extending between its supply and target compositions (Figure 7). Several useful insights can be gained from this diagram. Let us consider two MSAs; a and b, whose costs (\$/kg of recirculating MSA) are c_a and c_b. These costs can be converted into \$/kg of removed pollutant, c_a^r and c_b^r, as follows:

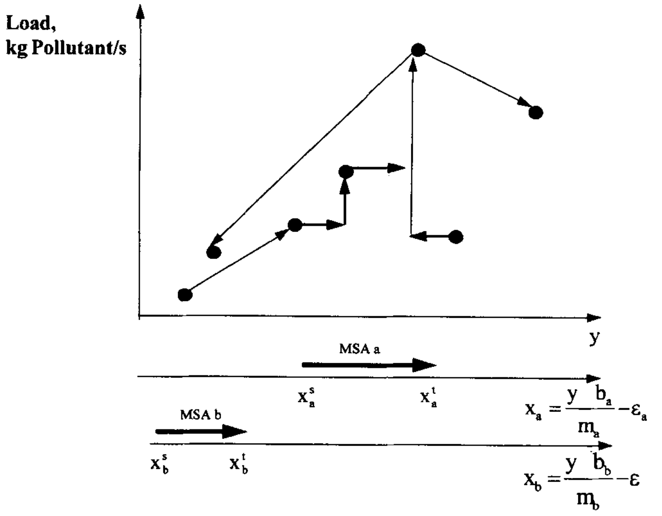

Figure 7. Using thermoeconomic insights to generate initial solutions.

$$c_a^r = \frac{c_a}{x_a^t - x_a^s} \quad (19a)$$

and

$$c_b^r = \frac{c_b}{x_b^t - x_b^s}. \quad (19b)$$

If arrow a lies completely to the left of arrow b and c_b^r is greater than c_a^r, one can eliminate MSA b from the mathematical formulation since it is thermodynamically and economically inferior to MSA a. Another shortcut observation can be inferred from the relative location of the sources and the MSAs. If an MSA lies to the right of a source node, the MSA is not a candidate for intercepting this node due to infeasibility of mass exchange. This observation is independent of other interceptions throughout the network since any interception will further move this node to the left.

We are now in a position to solve a case study using the proposed synthesis approach.

Case Study: Interception of Chloroethanol in an Ethyl Chloride Process

Ethyl chloride (C_2H_5Cl) can be manufactured by catalytically reacting ethanol and hydrochloric acid. Figure 8 is a simplified flow sheet of the process. First, ethanol is manufactured by the catalytic hydration of ethylene. Compressed ethylene is heated with water and reacted to from ethanol. Ethanol is separated using distillation followed by membrane separation (pervaporation). The aqueous waste from separa-

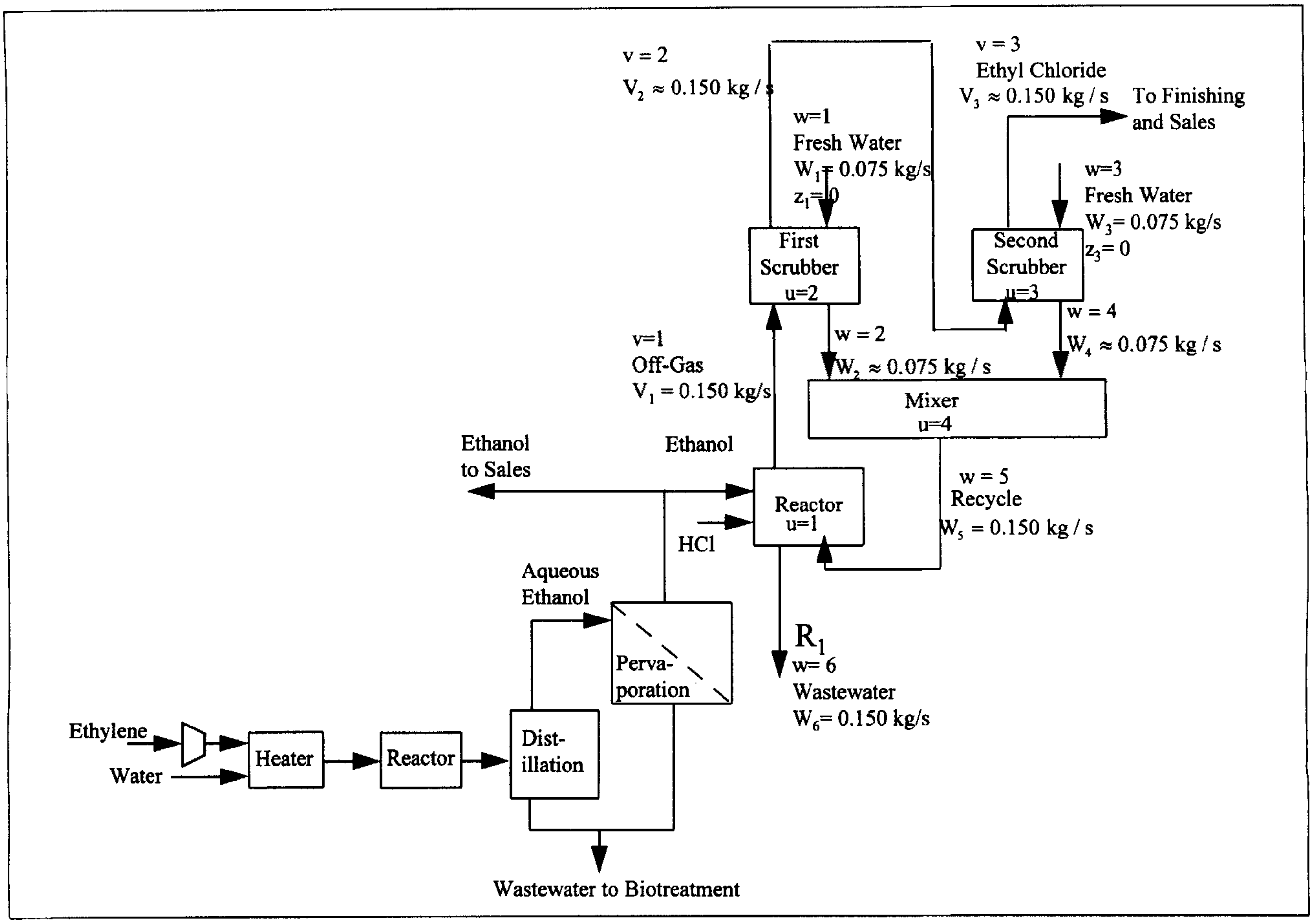

Figure 8. Simplified flowsheet of the ethyl chloride process.

tion is fed to a biotreatment unit in which the organic content of the wastewater is used as a bionutrient. This waste stream does not pose any environmental problems. The separated ethanol is reacted with hydrochloric acid in a multiphase reactor to form ethyl chloride. The reaction takes place primarily in the liquid phase. A by-product of the reaction is chloroethanol (CE) (also referred to as ethylene chlorohydrin, C_2H_5OCl). This side reaction will be referred to as the *oxychlorination reaction.* The rate of chloroethanol generation via oxychlorination (approximated by a pseudo-zero-order reaction) is given

$$r_{\text{oxychlorination}} = 6.03 \times 10^{-6} \text{ kg chloroethanol/s.} \quad (20)$$

While ethyl chloride is one of the least toxic of all chlorinated hydrocarbons, CE is a toxic pollutant (Sax and Lewis, 1986). The off-gas from the reactor is scrubbed with water in two absorption columns. The first column is intended to recover the majority of unreacted ethanol, hydrogen chloride, and CE. The second scrubber purifies the product from traces of unreacted materials and acts as a backup column in case the first scrubber is out of operation. Due to the very low solubility of ethyl chloride in water (0.45 wt/wt % at room temperature) and its high volatility (normal boiling point: 285 K), very little product is dissolved in water or condensed in the scrubber. Each scrubber contains two sieve plates and has an overall column efficiency of 65% (i.e., number of theoretical plates (NTP) = 1.3). Following the scrubber, ethyl chloride is finished and sold. The aqueous streams leaving the scrubbers are mixed and recycled to the reactor. A fraction of the CE recycled to the reactor is reduced to ethyl chloride. This side reaction will be referred to as the *reduction reaction.* The rate of this reaction can be approximated by the following pseudo-first-order expression:

$$r_{\text{reduction}} = 0.090\, z_5 \text{ kg chlorethanol/s.} \quad (21)$$

The compositions of CE in the gaseous and liquid effluents of the ethyl-chloride reactor are related through an equilibrium distribution coefficient as follows:

$$\frac{y_1}{z_6} = 5. \quad (22)$$

The aqueous effluent from the ethyl-chloride reactor, R_1, is environmentally unacceptable due to its content of CE. The objective of the WIN synthesis task is to optimally intercept chloroethanol-laden streams so as to reduce the chloroethanol content of R_1 to meet the following regulations:

Table 1. MSA Data That Can Remove CE from Gaseous Streams

Stream	Description	Supply Comp. (ppmw) x_j^s	Target Comp. (ppmw) x_j^t	m_j	ϵ_j (ppmw)	c_j ($/kg MSA)
SV_1	Polymeric resin	2	10	0.03	5	0.08
SV_2	Activated carbon	5	30	0.06	10	0.10
SV_3	Oil	200	300	0.80	20	0.05

Table 2. MSA Data That Can Remove CE from Liquid Streams

Stream	Description	Supply Comp. (ppmw) x_j^s	Target Comp. (ppmw) x_j^t	M_j	ϵ_j (ppmw)	c_j ($/kg MSA)
SW_1	Zeolite	3	15	0.09	15	0.70
SW_2	Air	0	10	0.10	100	0.05
SW_3	Steam	0	15	0.80	50	0.12

Target composition:

$$z_6^{\text{int}} = z_1^{\text{Terminal target}} \leq 7 \text{ ppmw}. \tag{23}$$

Target load:

$$\text{Load of CE in } R_1 \leq 1.05 \times 10^{-6} \text{ kg CE/s}. \tag{24}$$

Six MSAs are available for removing CE: three for gaseous streams and three for liquid streams. Tables 1 and 2 provide data for the MSAs.

Solution

This case study involves four units, three gaseous nodes, and six liquid nodes. The flow rates of all gaseous and liquid sources are shown in Figure 8. Also, the compositions of the two liquid nodes corresponding to entering fresh water are given ($z_1 = z_3 = 0$). The first step in the analysis is the development of the path-diagram equations to quantify the relationship of the seven unknown compositions. These equations are derived in Appendix C. The resulting mathematical description before interception (with all compositions in ppmw) is:

For $u = 1$:

$$0.180y_1 - 6.030 = 0.060z_5$$

$$y_1 - 5z_6 = 0.$$

For $u = 2$,

$$2y_2 + z_2 = 2y_1$$

$$y_2 = 0.10y_1.$$

For $u = 3$,

$$2y_3 + z_4 = 2y_2$$

$$y_3 = 0.10y_2.$$

For $u = 4$,

$$2z_5 = z_2 + z_4.$$

As has been previously mentioned, the gaseous path diagram for CE involves three unknown compositions (y_1, y_2, and y_3) while the liquid path diagram for CE has four unknown compositions (z_2, z_4, z_5, and z_6). The foregoing seven equations can be solved simultaneously to get the following compositions (in ppmw) prior to interception:

$$y_1 = 50.0$$

$$y_2 = 5.0$$

$$y_3 = 0.5$$

$$z_2 = 90.0$$

$$z_4 = 9.0$$

$$z_5 = 49.5$$

$$z_6 = 10.0.$$

In order to account for interception, Eqs. 10 and 11 are invoked to revise the foregoing equations. Therefore, the path-diagram equations following inteception become:

$$0.180y_1 - 6.030 = 0.060z_5^{\text{int}}$$

$$y_1 - 5z_6 = 0$$

$$2y_2 + z_2 = 2y_1^{\text{int}}$$

$$y_2 = 0.10y_1^{\text{int}}$$

$$2y_3 + z_4 = 2y_2^{\text{int}}$$

$$y_3 = 0.10y_2^{\text{int}}$$

$$2z_5 = z_2^{\text{int}} + z_4^{\text{int}}.$$

Next, we formulate the problem as described by program P1. The resulting MINLP was solved using the software GINO (Liebman et al., 1986). A solution was obtained in 25 CPU seconds on a Sun Sparcstation 10. The solution indicates that the optimal policy is to use activated carbon to intercept the gaseous stream leaving the reactor ($v = 1$) and reduced its composition to $y_1^{\text{int}} = 4.55$ ppmw (which corresponds to removing 4.57×10^{-6} kg CE/s from $v = 1$). The optimal solution has a minimum operating cost of approximately $576,000/yr based on 8,760 operating hours per annum.

It is worth pointing out that the MINLP formulation can be slightly expanded to generate a list of alternative options that are inferior to the optimal solution. For instance, by adding "cutting-plane" constraints (e.g., objective function ≥ $800,000), an alternative solution is generated. This option involves the use of air to strip CE from the effluent of the first scrubber followed by the application of zeolite to remove CE from the terminal wastewater stream. The cost of this option is $800,000/yr. When the constant in the cutting-plane constraint is increased to $825,000/yr, a new solution is generated. This solution involves the use of zeolite to remove 0.45×10^{-6} kg CE/s from the terminal wastewater stream (R_1

Table 3. Generated Solutions for the CE Case Study

Option	Intercepted Streams	Interception MSAs	Mass Removed (10^{-6} kg CE/s)	Oper. Cost ($/yr)
1	Off-gas from reactor ($v = 1$)	Activated carbon	4.57	576,163
2	Effluent from first scrubber ($w = 2$) and terminal wastewater (R_1 or $w = 6$)	Air followed by zeolite	1.31	800,000
3	Terminal wastewater (R_1 or $w = 6$)	Zeolite	0.45	827,820
4	Off-gas from reactor ($v = 1$)	Polymeric resin	4.57	1,440,407
5	Aqueous effluent from first scrubber ($w = 2$)	Air followed by zeolite	4.52	1,633,959
6	Aqueous effluent from mixer ($w = 5$)	Air followed by zeolite	4.52	2,100,692

or $w = 6$). This is the same solution that would have been obtained by applying the conventional MEN approach to the terminal wastewater stream. The operating cost of this solution is $827,820/yr, which is 44% more expensive than the optimal WIN solution. By successively eliminating the optimal solutions from the search space and solving the MINLP, we get the solutions ranked in Table 3.

Several observations can be drawn from the list of generated solutions:

- The WIN synthesis approach exploits the multimedia (multiphase) nature of the environmental problem. A gaseous stream was intercepted to solve a wastewater problem. This approach is critical, as the next generation of environmental regulations will no longer focus on an individual medium (e.g., clean air, clean water act, etc.). Instead, regulations will have to be enacted to address a chemical process as an integrated system with strong interactions among the gaseous and liquid emissions.
- The WIN synthesis approach is superior to the MEN synthesis approach. An in-plant stream was intercepted to affect the necessary changes in the terminal stream. Since the gaseous and liquid sources addressed by the WIN problem involve the terminal streams addressed by the MEN problem, any potential MEN solution is embedded in the wider spectrum of WIN solutions.
- More mass may be removed for less cost. This result can be explained based on thermodynamic and mass-transfer arguments. Removal of the pollutant from more concentrated streams is more thermodynamically favorable than removal from less concentrated streams. Therefore, it is typically less expensive to use low-cost MSAs to eliminate the pollutant from in-plant streams than it is to employ high-cost MSAs to remove traces of pollutant from the dilute terminal streams. It is also worth noting the nonlinear propagation of mass of the pollutant throughout the process. For a given effect on the pollutant content of a terminal stream, different masses may be removed from different in-plant streams. Another reason for this mass-cost observation is that removal of the pollutant in one medium can be less expensive than it is for another medium. For instance, a certain amount of the pollutant may be removed from air at a lower cost than it is to recover a smaller quantity from wastewater.

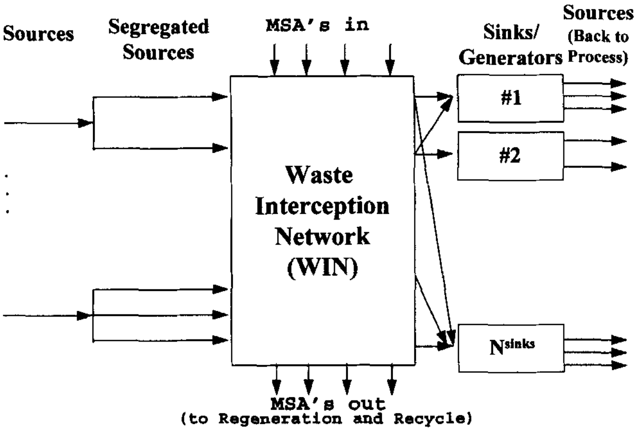

Figure 9. Global allocation of mass via segregation, interception.

Incorporation of WINs within a Mass-Integration Framework

Mass integration is aimed at the optimal allocation of species and streams throughout the process. In addition to stream interception, it also involves stream segregation, mixing, and recycle. Instead of dealing with the detailed flow sheet of the process, it is necessary to develop a representation that aids in systematizing mass allocation. The first step in conducting mass integration is the development of a global mass-allocation representation of the whole process (Figure 9). For each targeted species (e.g., pollutant), there are sources (streams that carry the species) and process sinks (units that can accept the species). Process sinks include reactors, heaters/coolers, biotreatment facilities, discharge media, and such. Streams leaving the sinks become, in turn, sources. Therefore, sinks are also generators of the targeted species.

Effective pollution prevention can be achieved by a combination of four strategies; stream segregation, interception, recycle from sources to sinks (with or without interception), and sink/generator manipulation. Each sink/generator may be manipulated via design and/or operating changes to affect flow rate and composition of what each sink/generator accepts and discharges. Manipulation of sinks/generators (which is beyond the scope of this article) includes chemical-based activities such as material substitution (e.g., Jobak, 1995; Constantinou et al., 1995), reaction alteration (Crabtree and El-Halwagi, 1995), and reactor network synthesis

(Lakshmanan and Biegler, 1995). Interception is tackled via a WIN. The following sections summarize the two other strategies of segregation and recycle.

Segregation

Segregation simply refers to avoiding the mixing of streams. In many cases, segregation of waste streams at the source renders several streams environmentally acceptable and hence reduces the pollution-prevention cost. Furthermore, segregation of streams with different compositions avoids unnecessary dilution of streams. This can lead to cost savings as a result of the reduced cost of removing the pollutant from the more concentrated streams. It may also lead to providing composition levels that allow the streams to be recycled directly to process units.

Recycle

Recycle refers to the utilization of a pollutant-laden stream (a source) in a process unit (a sink). A source may be recycled to a sink directly or following segregation and/or interception. Furthermore, multiple sources may be mixed prior to recycle. Typically, process constraints limit the range of pollutant composition and load that each sink can accept. These composition/load range constraints can be added to the optimization formulation provided in Appendix A. The solution of the extended MINLP provide the optimal interception, segregation and recycle strategies. The following example illustrates the integration of WINs with stream segregation and recycle.

Case Study Revisited: Segregation, Interception, and Recycle for the Chloroethanol Case Study

The scope of the previously addressed CE case study is now expanded to allow for stream segregation and recycle in addition to interception. There are four sinks ($u = 1$–4) and there is the potential for segregating two sources ($w = 2, 4$). Due to geographical limitations, the wastewater from the ethanol plant cannot be economically reused in the ethylchloride plant. The following process constraints should be considered:

$$\text{Composition of aqueous feed to reactor} \leq 65 \text{ ppmw CE} \tag{25}$$

$$\text{Composition of aqueous feed to first scrubber} \leq 8 \text{ ppmw CE} \tag{26}$$

$$\text{Composition of aqueous feed to second scrubber} \leq 0 \text{ ppmw CE} \tag{27}$$

$$0.090 \leq \text{flow rate of aqueous feed to reactor (kg/s)} \leq 0.150 \tag{28}$$

$$0.075 \leq \text{flow rate of aqueous feed to first scrubber (kg/s)} \leq 0.090 \tag{29}$$

$$0.075 \leq \text{flow rate of aqueous feed to second scrubber (kg/s)} \leq 0.085 \tag{30}$$

The following targets on composition and load are sought:

Target composition of terminal aqueous discharge

$$\leq \frac{z^{1^{\text{Original terminal target}}}}{3} = 3.3 \text{ ppmw} \tag{31}$$

Target load of CE in terminal aqueous discharge

$$\leq \frac{\text{original load of CE in terminal aqueous discharge}}{6} = 2.50 \times 10^{-7} \text{ kg CE/s.} \tag{32}$$

Solution

Since the flow rates of the streams fed to the sinks are to be determined as part of the optimization problem, the path equations derived in Appendix B are used without fixing the flow rates of the streams. Furthermore, constraints 25–32 are added to the MINLP formulation. The solution of this MINLP (shown in Figure 10) was obtained using the software GINO (Liebman et al., 1986) in 69 CPU seconds on a Sun Sparcstation 10. It indicates that the optimal policy is to segregate the effluents of the two scrubbers, recycle the aqueous effluent of the reactor to the first scrubber, and use activated carbon to intercept the gaseous stream leaving the first scrubber ($v = 2$) and reduce its composition to $y_2^{\text{int}} = 1.83$ ppmw. The annual operating cost of the system is approximately \$32,000/yr.

As has been mentioned before, the MINLP formulation can be slightly expanded by adding cutting-plane constraints to generate a list of alternative options that are inferior to the optimal solution. For instance, by fixing the process configuration and flows as indicated by the optimal solution and allowing the interception technology, load, and location to vary, the additional constraint of objective function ≥ \$150,000/yr yields an alternative solution is generated. This option involves the use of activated carbon to adsorb CE from the gaseous effluent of the reactor. The cost of this alternative is \$159,000/yr. When the constant in the cutting-plane constraint is increased to \$400,000/yr, a new alternative is identified, in which zeolite is used to remove CE from the effluent of the second scrubber. The cost of this solution is about \$439,000/yr.

Conclusions

This article introduced the new problem of synthesizing WINs to address in-plant separation of pollutants. This work also demonstrated the usefulness of employing WINs as in performing mass-integration analysis for pollution prevention. First, the path diagram was developed as a means of characterizing the global flow of the pollutant throughout the process. Next, the path diagram was integrated with the interception techniques using mass-exchange pinch diagrams. The WIN synthesis strategy was formulated as an MINLP whose solution yields the optimal interception locations, loads, and separating agents. This formulation was slightly revised to account for employing WINs in a mass-integration strategy that involves stream segregation and recycle in addition to interception. A case study was solved to elucidate the merits of the proposed approach and some intriguing results. It was also shown that pollution prevention is a multimedia

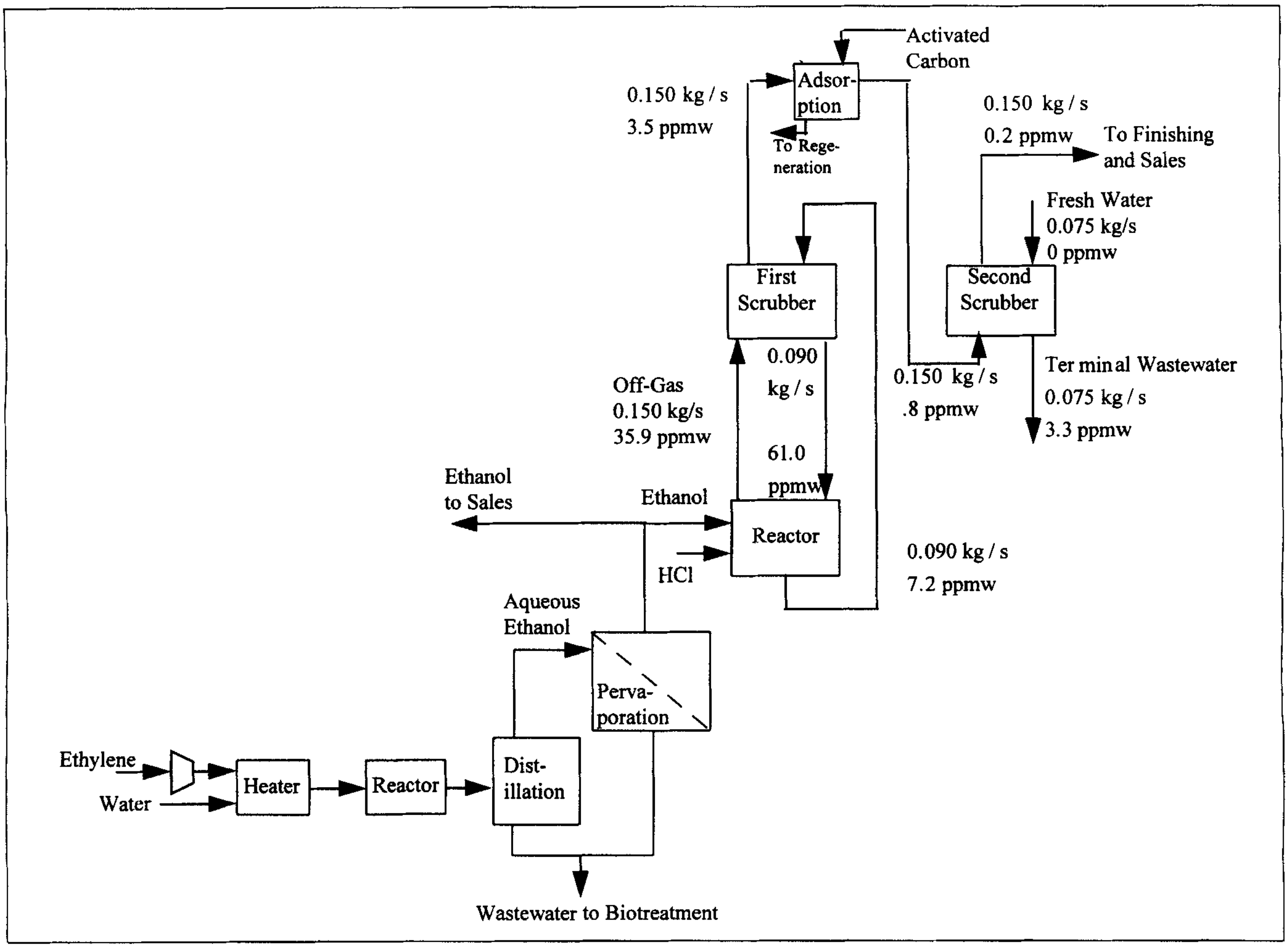

Figure 10. Optimal solution to the CE case study.

problem in which all phases should be simultaneously tackled. This is a more general understanding than the single-phase design approaches and environmental regulations. Furthermore, it was shown that more pollutant can be separated at lower cost when the optimal interception locations and loads are identified.

Acknowledgment

The financial support of the NSF (Grant NSF-NYI-CTS-9457013) is gratefully acknowledged.

Notation

b_j = intercept of equilibrium line for mass-separating agent j
m_j = slope of equilibrium line for mass-separating agent j
p = index of potential pinch-points for gaseous interception
P^{gas} = set of gaseous potential pinch points
P^{liquid} = set of liquid potential pinch points
q = index of potential pinch-points for liquid interception
x_j = mass fraction of pollutant in mass-separating agent j
x_j^s = supply composition of pollutant in mass-separating agent j for pollutant-laden gaseous streams
x_j^p = pinch composition of pollutant in mass-separating agent j for pollutant-laden gaseous streams
x_j^t = target composition of mass separating agent j for pollutant-laden gaseous streams
x_j^* = equilibrium outlet mass fraction of pollutant in mass-separating agent j
X_j^s = supply composition of pollutant in mass-separating agent j for pollutant-laden liquid streams
X_j^t = target composition of pollutant in mass-separating agent j for pollutant-laden liquid streams
y^p = composition of pollutant in gas phase at candidate pinch point p
z_w = composition of pollutant in liquid stream w
ϵ_j = minimum allowable composition for mass-separating agent j between equilibrium and operating lines
ϕ_a = mass generated of pollutant in the reactor

Subscripts and superscripts

i = waste stream i
q = potential liquid pinch point

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Appendix A: Pinch-Diagram Equations

As has been mentioned before, since the compositions of gaseous/liquid sources employed in the pinch diagrams are unknown, it is necessary to parametrize the rich composite stream as a function of path-diagram compositions. This parametrization can be achieved by extending the mixed-integer nonlinear representation proposed by El-Halwagi and Manousiouthakis (1990b) for regenerable MSAs to the situation of varying inlet and outlet compositions of rich streams. First, overall pollutant balances for the liquid and gaseous interception networks has to be realized. Therefore,

$$\sum_{\upsilon=1}^{NV} V_\upsilon(y_\upsilon - y_\upsilon^{\text{int}}) = \sum_{j=1}^{NSV} l_j\left(x_j^t - x_j^s\right) \tag{A1}$$

and

$$\sum_{w=1}^{NW} W_w(z_w - z_w^{\text{int}}) = \sum_{j=1}^{NSW} L_j\left(X_j^t - X_j^s\right). \tag{A2}$$

Next, material balances are written for the pollutant below potential pinch points. Since the pinch locations are not known, it is necessary to develop material balances that are applicable regardless of the pinch location. These balances are given by the following two equations for gaseous and liquid interceptions, respectively:

$$\sum_{\upsilon=1}^{NV} V_\upsilon\left[\lambda_{\upsilon,p}^{\text{int}}(y^p - y_\upsilon^{\text{int}}) - \lambda_{\upsilon,p}(y^p - y_\upsilon)\right]$$
$$-\sum_{j=1}^{NSV} l_j \eta_{j,p}^s\left(x_j^t - x_j^s\right) - \eta_{j,p}^t\left(x_j^p - x_j^t\right)\Big] \le 0 \qquad \forall p \epsilon \boldsymbol{P}^{\text{gas}} \tag{A3}$$

and

$$\sum_{w=1}^{NW} W_w\left[\gamma_{w,q}^{\text{int}}(z^q - z_w^{\text{int}}) - \gamma_{w,q}(z^q - z_w)\right]$$
$$-\sum_{j=1}^{NSW} L_j \beta_{j,q}^s\left(X_j^t - X_j^s\right) - \beta_{j,q}^t\left(X_j^q - X_j^t\right)\Big] \le 0$$
$$\forall q \in \boldsymbol{P}^{\textbf{liquid}}. \tag{A4}$$

These material balances are generally applicable due to the use of the binary coefficients $\lambda_{\upsilon,p}^{\text{int}}$, $\lambda_{\upsilon,p}$, $\eta_{j,p}^s$, $\eta_{j,p}^t$, $\gamma_{w,q}^{\text{int}}$, $\gamma_{w,q}$, $\beta_{j,q}^s$, and $\beta_{j,q}^t$. These coefficients play the role of selecting the proper load of each stream below the potential pinch points. They are defined as follows:

$$\left(2\lambda_{\upsilon,p}^{\text{int}} - 1\right)(y^p - y_\upsilon^{\text{int}}) \ge 0 \upsilon \in NV,\ p \in P^{\text{gas}},\ \lambda_{\upsilon,p}^{\text{int}} = 0/1 \tag{A5}$$

$$(2\lambda_{\upsilon,p} - 1)(y^p - y_\upsilon) \ge 0 \upsilon \in NV,\ p \in P^{\text{gas}},\ \lambda_{\upsilon,p} = 0/1 \tag{A6}$$

$$(2\eta_{j,p}^s - 1)(x_j^p - x_j^s) \ge 0 j \in SV,\ p \in P^{\text{gas}},\ \eta_{j,p}^s = 0/1 \tag{A7}$$

$$\left(2\eta_{j,p}^t - 1\right)\left(x_j^p - x_j^t\right) \ge 0 j \in SV,\ p \in P^{\text{gas}},\ \eta_{j,p}^t = 0/1 \tag{A8}$$

$$\left(2\gamma_{w,q}^{\text{int}} - 1\right)(z^q - z_w^{\text{int}}) \ge 0 w \in NW,\ q \in P^{\text{liquid}},\ \gamma_{w,q}^{\text{int}} = 0/1 \tag{A9}$$

$$(2\gamma_{w,q} - 1)(Z^q - Z_w) \geq 0 w \in NW,\ q \in P^{\text{liquid}},\ \gamma_{w,q} = 0/1 \tag{A10}$$

$$(2\beta^s_{j,q} - 1)(X^q_j - X^s_j) \geq 0 j \in SW,\ q \in P^{\text{liquid}},\ \beta^s_{j,q} = 0/1 \tag{A11}$$

$$\left(2\beta^t_{j,q} - 1\right)\left(X^q_j - X^t_j\right) \geq 0 j \in SW,\ q \in P^{\text{liquid}},\ \beta^t_{j,q} = 0/1. \tag{A12}$$

Equations A5–A12 correspond to the following definitions:

$$\lambda^{\text{int}}_{v,p} = \begin{cases} 1 & \text{if } y^{\text{int}}_v < y^p \quad v \in NV \\ 0 & \text{if } y^{\text{int}}_v \geq y^p \quad p \in P^{\text{gas}} \end{cases}$$

$$\lambda_{v,p} = \begin{cases} 1 & \text{if } y_v < y^p \quad v \in NV \\ 0 & \text{if } y_v \geq y^p \quad p \in P^{\text{gas}} \end{cases}$$

$$\eta^s_{j,p} = \begin{cases} 1 & \text{if } x^s_j < x^p_j \quad j \in SV \\ 0 & \text{if } x^s_j \geq x^p_j \quad p \in P^{\text{gas}} \end{cases}$$

$$\eta^t_{j,p} = \begin{cases} 1 & \text{if } x^t_j < x^p_j \quad j \in SV \\ 0 & \text{if } x^t_j \geq x^p_j \quad p \in P^{\text{gas}} \end{cases}$$

$$\gamma^{\text{int}}_{w,q} = \begin{cases} 1 & \text{if } z^{\text{int}}_w < z^q \quad w \in NW \\ 0 & \text{if } z^{\text{int}}_w \geq z^q \quad q \in P^{\text{liquid}} \end{cases}$$

$$\gamma_{w,q} = \begin{cases} 1 & \text{if } z_w < z^q \quad w \in NW \\ 0 & \text{if } z_w \geq z^q \quad q \in P^{\text{liquid}} \end{cases}$$

$$\beta^s_{j,q} = \begin{cases} 1 & \text{if } X^s_j < X^q_j \quad j \in SW \\ 0 & \text{if } X^s_j \geq X^q_j \quad q \in P^{\text{liquid}} \end{cases}$$

$$\beta^t_{j,q} = \begin{cases} 1 & \text{if } X^t_j < X^q_j \quad j \in SW \\ 0 & \text{if } X^t_j \geq X^q_j \quad q \in P^{\text{liquid}} \end{cases}$$

Depending on the relative location of the stream, these binary coefficients adjust the load of the stream below the pinch to its proper value.

Appendix B: Mathematical Formulation

The following is the mathematical formulation for minimizing the operating cost of the WIN:

$$\min \sum_{j=1}^{NSV} c_j l_j + \sum_{j=1}^{NSW} C_j L_j. \tag{B1}$$

Subject to

Path-diagram constraints

$$\sum_{v \in \text{GAS\_INPUTS}_u} V_v + \sum_{w \in \text{LIQUID\_INPUTS}_u} W_w = \sum_{v \in \text{GAS\_OUTPUTS}_u} V_v + \sum_{w \in \text{LIQUID\_OUTPUTS}_u} W_w \quad u \in \textbf{UNIT}$$

$$\sum_{v \in \text{GAS\_INPUTS}_u} V_v y_v^{\text{int}} + \sum_{w \in \text{LIQUID\_INPUTS}_u} W_w z_w^{\text{int}} = \sum_{v \in \text{GAS\_OUTPUTS}_u} V_v y_v + \sum_{w \in \text{LIQUID\_OUTPUTS}_u} W_w z_w - \text{Net}_u \quad u \in \textbf{UNITS}$$

$$f_u(\Phi^{\text{int}}_v,\ y^{\text{int}}_v,\ \Psi^{\text{int}}_w,\ z^{\text{int}}_w : v \in \text{GAS\_INPUTS}_u \text{ and } w \in \text{LIQUID\_INPUTS}_u) = (\Phi_v,\ y_v,\ \Psi_w,\ z_w : v \in \text{GAS\_OUTPUTS}_u \text{ and } w \in \text{LIQUID\_OUTPUTS}_u) \quad u \in \textbf{UNITS}.$$

Pinch-diagram constraints

$$\sum_{v=1}^{NV} V_v(y_v - y^{\text{int}}_v) = \sum_{j=1}^{NSV} l_j\left(x^t_j - x^s_j\right)$$

$$\sum_{w=1}^{NW} W_w(z_w - z^{\text{int}}_w) = \sum_{j=1}^{NSW} L_j\left(X^t_j - X^s_j\right)$$

$$\sum_{v=1}^{NV} V_v\left[\lambda^{\text{int}}_{v,p}(y^p - y^{\text{int}}_v) - \lambda_{v,p}(y^p - y_v)\right] - \sum_{j=1}^{NSV} l_j \eta^s_{j,p}\left(x^t_j - x^s_j\right) - \eta^t_{j,p}\left(x^p_j - x^t_j\right) \leq 0 \qquad \forall p \in \boldsymbol{P}^{\textbf{gas}}$$

$$\sum_{w=1}^{NW} W_w\left[\gamma^{\text{int}}_{w,q}(z^q - z^{\text{int}}_w) - \gamma_{w,p}(z^q - z_w)\right] - \sum_{j=1}^{NSW} L_j \beta^s_{j,q}\left(X^t_j - X^s_j\right) - \beta^t_{j,q}\left(X^q_j - X^t_j\right) = \leq 0 \qquad \forall q \in \boldsymbol{P}^{\textbf{liquid}}$$

along with the definitions of the binary coefficients $\lambda^{\text{int}}_{v,p}$, $\lambda_{v,p}$, $\eta^s_{j,p}$, $\eta^t_{j,p}$, $\gamma^{\text{int}}_{w,q}$, $\gamma_{w,q}$, $\beta^s_{j,q}$, and $\beta^t_{j,q}$ (Eqs. A5–A12).

Environmental regulations

$$y_i^{\text{Terminal target}} \leq y_i^{\text{Terminal reg}} \qquad i = 1, 2 \ldots, Nr^{\text{gas}}$$

$$z_i^{\text{Terminal target}} \leq z_i^{\text{Terminal reg}} \qquad i = NR^{\text{gas}} + 1, NR^{\text{gas}} + 2, \ldots, NR^{\text{gas}} + NR^{\text{liquid}}$$

$$\sum_{i=1}^{NR^{\text{gas}}} V_i^{\text{Terminal}} y_i^{\text{Terminal target}} \leq (1 - \alpha^{\text{gas}}) \sum_{i=1}^{NR^{\text{gas}}} V_i^{\text{Terminal}}\ y_i^{\text{Terminal}}$$

$$\sum_{i=NR^{\text{gas}}+1}^{NR^{\text{gas}}+NR^{\text{liquid}}} W_i^{\text{Terminal}} z_i^{\text{Terminal target}} \leq (1 - \alpha^{\text{liquid}}) \sum_{i=NR^{\text{gas}}+1}^{NR^{\text{gas}}+NR^{\text{liquid}}} W_i^{\text{Terminal}} z_i^{\text{Terminal}}.$$

Appendix C: Derivation of the Path-Diagram Equations for the Chloroethanol Case Study

In the chloroethanol case study there are four units processing the pollutant, three gaseous sources, and six liquid sources. As shown by Figure 7, overall material balances around the four units ($u = 1$–4, assuming constant flow rate of carriers) provide the flow rates of the carrier gas and liquid to be:

$$V_1 = V_2 = V_3 = 0.150 \text{ kg/s}$$
$$W_1 = W_2 = W_3 = W_4 = 0.075 \text{ kg/s}$$
$$W_5 = W_6 = 0.150 \text{ kg/s}.$$

Component material balance for chloroethanol around the reactor (u = 1)

Chloroethanol in recycled reactants + chloroethanol generated due to oxychlorination reaction = chloroethanol in off-gas + chloroethanol in wastewater W_i + chloroethanol depleted by reduction reaction. (C1)

Hence

$$W_5 z_5 + 6.03\times 10^{-6} = V_1 y_1 + W_6 z_6 + 0.09 z_5. \qquad \text{(C2)}$$

But, as discussed in the problem statement, the compositions of CE in the gaseous and liquid effluents of the ethyl-chloride reactor are related through an equilibrium distribution coefficient as follows:

$$\frac{y_1}{z_6} = 5. \qquad \text{(C3)}$$

Therefore, Eq. C2 can be further simplified by invoking Eq. C3 and substituting for the numerical values of V_1, W_5, and W_6 to get

$$0.180 y_1 - 0.060 z_5 = 6.03\times 10^{-6} \qquad \text{(C4)}$$

with y_1 and z_5 in mass fraction units. Therefore, the previous equation can be rewritten as

$$0.180 y_1 - 0.060 z_5 = 6.030, \qquad \text{(C5)}$$

with y_1 and z_5 in units of ppmw.

Component material balance for chloroethanol around first scrubber (u = 2)

$$V_1 y_1 + W_1 z_1 = V_2 y_2 + W_2 z_2. \qquad \text{(C6)}$$

Substituting for the values of V_1, V_2, W_1, and W_2 and noting that z_1 is zero (fresh water), we get

$$2(y_1 - y_2) - z_2 = 0. \qquad \text{(C7)}$$

The Kremser equation can be used to model the scrubber.

$$\text{NTP} = \frac{\ln\left[\left(1 - \frac{HV_1}{W_1}\right)\left(\frac{y_1 - Hz_1}{y_2 - Hz_1}\right) + \frac{HV_1}{W_1}\right]}{\ln\left(\frac{W_1}{HV_1}\right)}, \qquad \text{(C8)}$$

where Henry's coefficient $(H) = 0.1$ and $\text{NTP} = 1.3$. Therefore,

$$1.3 = \frac{\ln\left(0.8\frac{y_1}{y_2} + 0.2\right)}{\ln(5)},$$

that is,

$$y_2 = 0.10 y_1. \qquad \text{(C9)}$$

Similar to Eqs. C7 and C9, one can derive the following two equations for the second scrubber ($u = 3$):

$$2(y_2 - y_3) - z_4 = 0 \qquad \text{(C10)}$$

and

$$y_3 = 0.10 y_2. \qquad \text{(C11)}$$

Component material balance for chloroethanol around the mixer (u = 4)

$$W_2 z_2 + W_4 z_4 = W_5 z_5. \qquad \text{(C12)}$$

By plugging the values of W_1, W_2 and W_3 into Eq. C12, we get

$$z_2 + z_4 - 2 z_5 = 0. \qquad \text{(C13)}$$

Manuscript received Dec. 4, 1995, and revision received Apr. 26, 1996.