Synthesis of Reactive Mass-Exchange Networks with General Nonlinear Equilibrium Functions

B. K. Srinivas and M. M. El-Halwagi
Chemical Engineering Dept., Auburn University, Auburn, AL 36849

The problem of synthesizing reactive mass-exchange networks (REAMENs) is addressed for which the equilibrium relations governing the transfer of a certain species from rich streams to reactive mass-separating agents are nonlinear (convex and/or nonconvex). Previously developed synthesis procedures for REAMENs are not applicable to such cases, since they were developed for cases of linear and/or convex equilibria. Two peculiar phenomena are associated with REAMENs with general nonlinear equilibria: the location of a mass-exchange pinch point is not restricted to supply compositions of streams; mass exchangers may straddle the pinch point even for networks featuring the minimum cost of mass-separating agents. To account for such intriguing characteristics, a systematic procedure is developed to synthesize cost-effective REAMENs with general nonlinear equilibria. In addition, a robust solution procedure is devised to guarantee the identification of the global solution of the developed optimization programs. Applicability and usefulness of the proposed synthesis procedure are demonstrated via a case study on the desulfurization of gaseous wastes from a coal-to-methanol plant.

Introduction

In recent years, increased environmental awareness and regulations have spurred a growing interest in the development of economically sustainable waste-reduction technologies. An efficient approach toward this direction is to recover the undesirable species in their original forms or to convert them by chemical reactions to some other forms of products that may be reusable or resalable. In this context, the novel notion of synthesizing physical mass-exchange networks (MENs) was introduced by El-Halwagi and Manousiouthakis (1989) for the identification of a cost-effective network of mass exchangers to selectively transfer certain species from a set of rich streams to a set of physical mass-separating agents (MSAs) (or lean streams). Systematic techniques have been developed to address several important categories of physical MEN synthesis with linear equilibrium relations. These include graphical techniques and optimization-based procedures (El-Halwagi and Manousiouthakis, 1989; 1990a,b). These techniques provide systematic tools for the selection of optimal MSAs, flow rates and system configuration. They also identify thermodynamic bottlenecks (pinch points) that limit the extent of separation. Recently, the problem of synthesizing reactive mass exchange networks (REAMENs) (El-Halwagi and Srinivas, 1992) has been introduced. The principal objective of synthesizing REAMENs is to preferentially transfer certain species from a set of rich streams to a set of reactive MSAs, whereby the undesirable species may be converted into other chemical forms. A linear programming formulation was devised to tackle REAMEN problems with linear or convex equilibrium relations.

When the equilibrium distribution functions that govern the transfer of the undesirable species from the rich streams to the MSAs are linear or convex, it has been shown (El-Halwagi and Manousiouthakis, 1990b; El-Halwagi and Srinivas, 1992) that the location of the most constrained region for the network design, the pinch point, corresponds only to the supply composition of a stream into the network. Hence, by simply checking over all supply compositions, it is possible to identify the pinch point and the minimum cost of MSAs required to perform the specified separation task. However, the equilibrium relations governing the transfer of a certain species from a rich stream to a reactive MSA can, in general, be nonconvex. Consequently, the location of the pinch point is not limited to the supply compositions of the streams. This entails the need to search over an infinite number of compositions. In such cases, none of the previously-developed MEN/REAMEN synthesis techniques is applicable.

This article develops a systematic technique for the synthesis

of REAMENs with general nonlinear equilibrium relations (convex and/or nonconvex). A two-stage procedure will be developed to synthesize cost-effective REAMENs. In the first stage, the minimum cost of MSAs is identified without any commitment to the final network structure. The second stage is aimed at minimizing the number of mass exchangers while realizing the minimum cost of MSAs. It will be shown that reactive mass-exchange pinch points do not necessarily correspond to the inlets of streams into the network, and consequently a new algorithm is developed to locate the pinch and minimize the cost of MSAs. In addition, it will be demonstrated that even for networks featuring minimum cost of MSAs, a mass exchanger can straddle the pinch. The effect of such intriguing phenomena, which differ from those of MENs/REAMENs with linear or convex equilibrium, will be incorporated within the synthesis technique. Examples will depict the usefulness of the devised approach.

Background

In this section, some of the basic tools of the REAMEN synthesis with linear and/or convex equilibrium functions are discussed along with the limitations of these tools in tackling REAMEN problems with nonconvex equilibriums. Owing to the combinatorics of the problem, a decomposition approach with a two-stage targeting procedure can be efficiently adopted. In the first stage, the minimum cost of MSAs required to perform the specified mass-exchange task is identified. This target aims at minimizing the operating cost of the network. In the second stage, the minimum number of mass-exchange units which can realize the minimum cost of MSAs solution is generated. This target attempts to minimize the fixed cost of the network.

For the minimum cost of MSAs, mass-exchange pinch points (or thermodynamic bottlenecks) in the network have to be identified (El-Halwagi and Manousiouthakis, 1989; El-Halwagi and Srinivas, 1992). The pinch diagram is constructed by plotting the mass exchanged by each stream vs. its composition scale. Composition scales are mapped via a one-to-one correspondence that employs equilibrium relations with a minimum mass-exchange driving force. Superposition is then used to create a rich- and a lean-composite stream. The point at which both composite streams touch is called the pinch point. The pinch point decomposes the REAMEN into two sections: a rich end (above the pinch) and a lean end (below the pinch). It has been shown (El-Halwagi and Manousiouthakis, 1990b; El-Halwagi and Srinivas, 1992) that for mass-exchange operations with MSAs exhibiting linear and/or convex equilibrium relationships, the pinch points correspond only to the inlets of any rich/lean stream, excluding the inlet points that fall outside the composition range shared by both composite streams. As mentioned previously, for reactive MSAs the equilibrium relations are not necessarily linear or convex. In the following sections, a systematic procedure will be developed to address the systematic task with such general nonlinear equilibria.

Problem Characteristics

Problem statement

Given a set $R=\{i \mid i=1, NR\}$ of rich streams and a set $S=\{j \mid j=1, NS\}$ of MSAs (both physical and reactive), synthesize a cost-effective REAMEN which can preferentially transfer a certain component from the rich streams to the MSAs. Given also are the supply and target compositions of all the rich streams and the MSAs. The flow rates of the rich streams are also known.

Pinch location

Let us consider the following equilibrium distribution function which represents the transfer of a certain species from a rich stream to the jth MSA:

$$y^* = f_j(x_j^*) \tag{1}$$

Let the function $f_j(x_j)$ be a continuous and differential monotone. Hence, for a given y and a given minimum allowable composition difference, ϵ_j, the maximum attainable composition in the jth lean stream is given by:

$$x_j = \phi_j(y) - \epsilon_j \tag{2a}$$

where $\phi_j(y)$ is the inverse of the equilibrium function:

$$\phi_j(y) = f_j^{-1}(y) \tag{2b}$$

Equation 2a can now be used to construct a one-to-one correspondence among all the compositions of the rich streams and the MSAs for which mass exchange is thermodynamically feasible.

Consider the transfer of a single component from two rich streams, R_1 and R_2, to two MSAs, S_1 and S_2. Let the supply and target compositions of the transferable component in R_1 and R_2 be (y_1^s, y_1^t) and (y_2^s, y_2^t), respectively, and let the flow rates of R_1 and R_2 be G_1 and G_2, respectively. Also, let the supply and target compositions of the transferable component in S_1 and S_2 be (x_1^s, x_1^t) and (x_2^s, x_2^t), respectively. If the optimal flow rates of the two MSAs are known to be L_1 and L_2, one can represent the rich and the lean streams on the pinch diagram, as shown in Figure 1a. Hence, by employing superposition a rich- and a lean-composite stream are created and touched at the pinch point. As can be seen from Figure 1b, the pinch location does not correspond to either the supply or target composition of any stream. This situation is a deviation from the cases of MENs/REAMENs with linear or convex equilibria. Therefore, a novel approach is needed to tackle the synthesis of REAMENs with general nonlinear equilibria. In the sequel, we develop a mathematical formulation to minimize the cost of MSAs for REAMENs with general nonlinear equilibria. The first step in our approach is to devise a mathematical description of the characteristics defining the synthesis problem.

Problem Features

In general, the optimal flow rates of the MSAs are not known beforehand. Hence, in order to identify them along with the pinch location, a mathematical expression representing the mass exchanged by the lean-composite stream as a function of flow rates and compositions of the lean streams is needed. Note that this expression will vary depending on the existence/absence of lean streams within composition ranges. Hence,

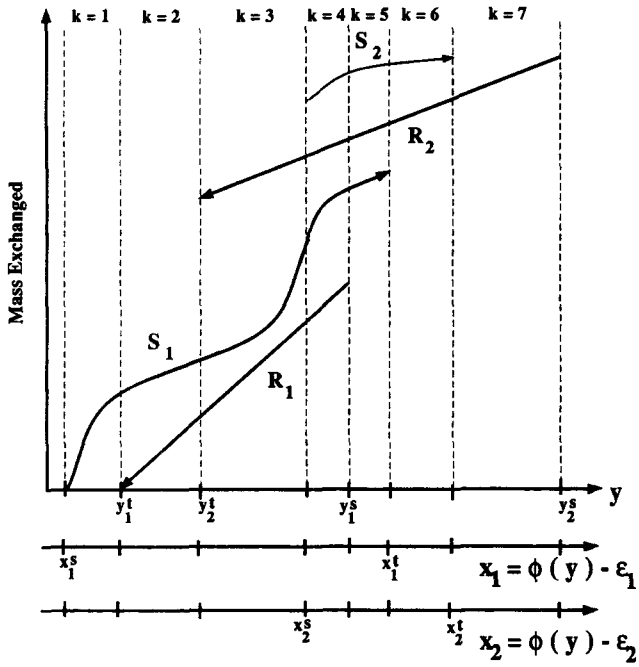

Figure 1a. Reactive mass-exchange representation for general nonlinear equilibria.

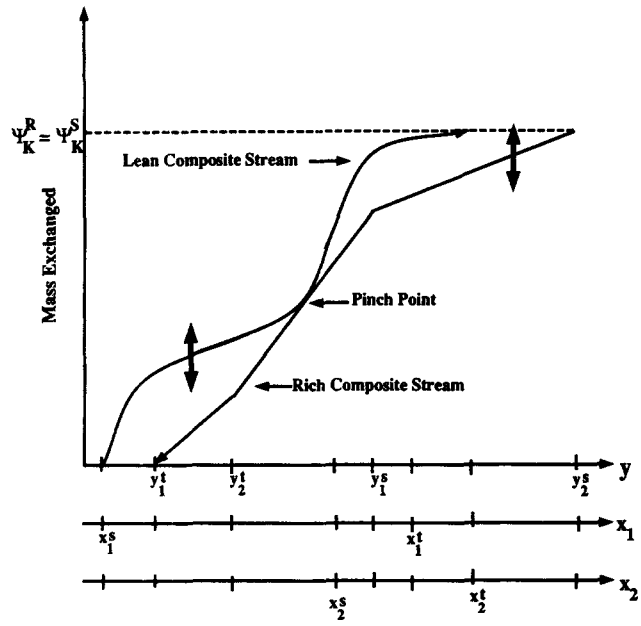

Figure 1b. Pinch diagram for general nonlinear REAMEN.

one can divide the entire composition range into $K = 2NR + 2NS - 1$ intervals that correspond to the inlets and outlets of the rich and the lean streams, as shown in Figure 1a. The value of the rich scale corresponding to the end of the kth interval is denoted by $\bar{y}_k$ where k ranges from 1 to K. Similarly, the composition of the jth MSA corresponding to the end of the kth interval is designated as $\bar{x}_{j,k}$ where $k = 1, 2, \ldots, K$. We also need to define the following sets:

$$R_k = \{i \mid \text{rich stream } i \text{ passes through interval } k\} \quad (3a)$$

$$S_k = \{j \mid \text{lean stream } j \text{ passes through interval } k\} \quad (3b)$$

In the sequel, we develop mathematical expressions to describe the mass exchanged by the rich- and the lean-composite streams for each composition interval, ψ_k^R and ψ_k^S, respectively. Hence, for the rich streams we can write the following:

• Cumulative mass lost by all the rich streams until an arbitrary composition, y_k, within the kth interval:

$$\psi_k^R(y_k) = \psi_{k-1}^R(\bar{y}_{k-1}) + \sum_{i \in R_k} G_i(y_k - \bar{y}_{k-1})$$

$$k = 1, 2, \ldots, K \quad (4)$$

where

$$\bar{y}_{k-1} \le y_k \le \bar{y}_k \quad (5)$$

$$\psi_0^R(\bar{y}_0) = 0 \quad (6)$$

and the total mass lost by all the rich streams:

$$\psi_K^R(\bar{y}_K) = \sum_{i \in R} G_i(y_i^s - y_i^t) \quad (7)$$

Since the flow rates of all rich streams are known, for any y_k the corresponding value of $\psi_k^R(y_k)$ can be readily calculated via Eq. 4.

We can also write an equivalent set of equations for the lean streams. Hence, the cumulative mass gained by all the lean streams until an arbitrary set of equivalent compositions ($x_{1,k}$, $x_{2,k}$, ..., $x_{NS,k}$) within the kth interval can be expressed as:

$$\psi_k^S(x_{1,k}, x_{2,k}, \ldots, x_{NS,k}, L_1, L_2, \ldots, L_{NS}) = \psi_{k-1}^S(\bar{x}_{1,k-1}, \bar{x}_{2,k-1}, \ldots, \bar{x}_{NS,k-1}, L_1, L_2, \ldots, L_{NS}) + \sum_{j \in S_k} L_j(x_{j,k} - \bar{x}_{j,k-1})$$

$$k = 1, 2, \ldots, K \quad (8)$$

where

$$\bar{x}_{j,k-1} \le x_{j,k} \le \bar{x}_{j,k} \quad j = 1, 2, \ldots, NS;\ k = 1, 2, \ldots, K \quad (9)$$

Equation 8 may be mapped onto the y scale by using Eq. 2a to yield:

$$\psi_k^S(y_k, L_1, L_2, \ldots, L_{NS}) = \psi_{k-1}^S(\bar{y}_{k-1}, L_1, L_2, \ldots, L_{NS}) + \sum_{j \in S_k} L_j[\phi_j(y_k) - \epsilon_j - \bar{x}_{j,k-1}] \quad k = 1, 2, \ldots, K \quad (10)$$

where

$$\psi_0^S(\bar{y}_0, L_1, L_2, \ldots, L_{NS}) = 0 \quad (11)$$

and

$$\psi_K^S(\bar{y}_K, L_1, L_2, \ldots, L_{NS}) = \sum_{j \in S} L_j(x_j^t - x_j^s) \quad (12)$$

Since material balance has to be satisfied, then

$$\psi_K^S(\bar{y}_K, L_1, L_2, \ldots, L_{NS}) = \psi_K^R(\bar{y}_K) \tag{13}$$

In order to guarantee thermodynamic feasibility of mass exchange, the lean-composite stream must be above the rich composite stream at each composition. One way of insuring this is to require that within any composition interval the least vertical distance between the lean- and the rich-composite streams is nonnegative. Hence, we may write:

$$\min_{\bar{y}_{k-1} \le y_k \le \bar{y}_k} \{\psi_k^S(y_k, L_1, L_2, \ldots, L_{NS}) - \psi_k^R(y_k)\} \ge 0 \quad k = 1, 2, \ldots, K \tag{14}$$

Having developed the necessary mathematical expressions to calculate the mass lost and gained by the rich and the lean streams over the entire range of operating concentration, and the conditions for thermodynamic feasibility, we can now formulate the problem of minimizing the cost of MSAs as described in the following section.

Minimum Cost of MSAs

Mathematical formulation

In this section, we develop an optimization program whose objective is to minimize the cost of MSAs while satisfying all necessary material-balance and thermodynamic constraints. Let the unit cost of the jth MSA (primarily cost of regeneration and makeup, \$/kg of recirculating MSA) be denoted by c_j. Hence, the objective function can be expressed as follows:

$$\min \sum_{j \in S} c_j L_j \tag{P1}$$

subject to the following constraints (which are based on Eqs. 4-14):

- Overall material balance constraints:

$$\psi_0^R(\bar{y}_0) = \psi_0^S(\bar{y}_0) = 0$$

$$\psi_K^R(\bar{y}_K) - \psi_K^S(\bar{y}_K, L_1, L_2, \ldots, L_{NS}) = 0$$

where

$$\psi_K^R(\bar{y}_K) = \sum_{i \in R} G_i(y_i^s - y_i^t)$$

and

$$\psi_K^S(\bar{y}_K, L_1, L_2, \ldots, L_{NS}) = \sum_{j \in S} L_j(x_j^t - x_j^s)$$

- Thermodynamic feasibility constraints:

$$\min_{\bar{y}_{k-1} \le y_k \le \bar{y}_k} \{\psi_k^S(y_k, L_1, L_2, \ldots, L_{NS}) - \psi_k^R(y_k)\} \ge 0 \quad k = 1, 2, \ldots, K$$

where

$$\psi_k^R(y_k) = \psi_{k-1}^R(\bar{y}_{k-1}) + \sum_{i \in R_k} G_i(y_k - \bar{y}_{k-1}) \quad k = 1, 2, \ldots, K$$

and

$$\psi_k^S(y_k, L_1, L_2, \ldots, L_{NS}) = \psi_{k-1}^S(\bar{y}_{k-1}, L_1, L_2, \ldots, L_{NS}) + \sum_{j \in S_k} L_j[\phi_j(y_k) - \epsilon_j - \bar{x}_{j,k-1}] \quad k = 1, 2, \ldots, K$$

Also:

$$\bar{y}_{k-1} \le y_k \le \bar{y}_k$$

- Resource availability constraints:

$$0 \le L_j \le L_j^c, \quad j \in S$$

In the following section, we devise a procedure for the global optimization of program P1.

Solution procedure

The primary difficulty in solving program P1 stems from the thermodynamic feasibility constraints that are described by Eq. 14. One can replace each of these K constraints by the following conditions:

$$\psi_k^S(y_k, L_1, L_2, \ldots, L_{NS}) - \psi_k^R(y_k) \ge 0 \tag{15}$$

for each y_k in the kth composition interval.

Equation 15 corresponds to an infinite number of constraints. One may create a relaxed version of P1 by writing Eq. 15 for a finite number of y_ks that represent a subset of the infinite number of y_ks lying between $\bar{y}_{k-1}$ and $\bar{y}_k$. Let's denote this finite number by N_{iter} and designate the values of these y_ks by $\hat{y}_k^r$ where $r = 1, 2, \ldots, N_{\text{iter}}$. Hence, one obtains the following relaxed program:

$$\min \sum_{j \in S} c_j L_j \tag{RP1}$$

subject to

$$\psi_0^R(\bar{y}_0) = \psi_0^S(\bar{y}_0) = 0$$

$$\psi_K^R(\bar{y}_K) - \psi_K^S(\bar{y}_K, L_1, L_2, \ldots, L_{NS}) = 0$$

where

$$\psi_K^R(\bar{y}_K) = \sum_{i \in R} G_i(y_i^s - y_i^t)$$

$$\psi_K^S(\bar{y}_K, L_1, L_2, \ldots, L_{NS}) = \sum_{j \in S} L_j(x_j^t - x_j^s)$$

$$\psi_k^S(\hat{y}_k^r, L_1, L_2, \ldots, L_{NS}) - \psi_k^R(\hat{y}_k^r) \ge 0 \quad \begin{matrix} k = 1, 2, \ldots, K \\ r = 1, 2, \ldots, N_{\text{iter}} \end{matrix}$$

where

$$\psi_k^R(\hat{y}_k^r) = \psi_{k-1}^R(\bar{y}_{k-1}) + \sum_{i \epsilon R_k} G_i(\hat{y}_k^r - \bar{y}_{k-1}) \quad \begin{matrix} k=1, 2, \ldots, K \\ r=1, 2, \ldots, N_{\text{iter}} \end{matrix}$$

$$\psi_k^S(\hat{y}_k^r, L_1, L_2, \ldots, L_{NS}) = \psi_{k-1}^S(\bar{y}_{k-1}, L_1, L_2, \ldots, L_{NS}) + \sum_{j \epsilon S_k} L_j[\phi_j(\hat{y}_k^r) - \epsilon_j - \bar{x}_{j,k-1}] \quad \begin{matrix} k=1, 2, \ldots, K \\ r=1, 2, \ldots, N_{\text{iter}} \end{matrix}$$

and

$$\bar{y}_{k-1} \le \hat{y}_k^r \le \bar{y}_k \quad \begin{matrix} k=1, 2, \ldots, K \\ r=1, 2, \ldots, N_{\text{iter}} \end{matrix}$$

$$0 \le L_j \le L_j^c, \quad j \epsilon S$$

Since all compositions $\hat{y}_k^r$ (where $k=1, 2, \ldots, K$ and $r=1, 2, \ldots, N_{\text{iter}}$) are fixed, the above program (RP1) is linear. The solution of the relaxed problem RP1 (which is denoted by $\hat{L}_1^{N_{\text{iter}}}, \hat{L}_2^{N_{\text{iter}}}, \ldots, \hat{L}_{NS}^{N_{\text{iter}}}$) provides an objective function that is a lower bound on the optimal objective function of the original program P1. This is attributed to the fact that RP1 has only a subset of the infinite constraints of P1. Therefore, if the solution of RP1 satisfies all the constraints of P1, then it is also the optimal solution of P1. However, if any of the constraints of P1 are not satisfied, additional constraints must be added to RP1 by writing the thermodynamic-feasibility constraints described by Eq. 15 for further points of y_k. An efficient way of selecting values for additional y_ks is by identifying those y_ks at which the thermodynamic-feasibility constraints are violated the most. Based on the foregoing notions, we can now present the steps of a robust algorithm for obtaining the global solution of P1:

(1) Within each composition interval, select an arbitrary value for $\hat{y}_k^1$ such that:

$$\bar{y}_{k-1} \le \hat{y}_k^1 \le \bar{y}_k \qquad k=1, 2, \ldots, K \tag{16}$$

(2) Set $N_{\text{iter}} = 1$

(3) Solve the linear program RP1 to obtain flow rates of the MSAs. Denote these flow rates by $\hat{L}_1^{N_{\text{iter}}}, \hat{L}_2^{N_{\text{iter}}}, \ldots, \hat{L}_{NS}^{N_{\text{iter}}}$.

(4) Check the thermodynamic feasibility of the solution obtained in step 3 by solving the following K independent optimization problems. For each k (where $k=1, 2, \ldots, K$) solve the following problem:

$$\min \alpha_k \tag{AP$_k$}$$

subject to

$$\psi_k^S(y_k, \hat{L}_1^{N_{\text{iter}}}, \hat{L}_2^{N_{\text{iter}}}, \ldots, \hat{L}_{NS}^{N_{\text{iter}}}) - \psi_k^R(y_k) = \alpha_k$$

where

$$\psi_k^R(y_k) = \psi_{k-1}^R(\bar{y}_{k-1}) + \sum_{i \epsilon R_k} G_i(y_k - \bar{y}_{k-1})$$

$$\psi_k^S(y_k, \hat{L}_1^{N_{\text{iter}}}, \hat{L}_2^{N_{\text{iter}}}, \ldots, \hat{L}_{NS}^{N_{\text{iter}}}) = \psi_{k-1}^S(\bar{y}_{k-1}, \hat{L}_1^{N_{\text{iter}}}, \hat{L}_2^{N_{\text{iter}}}, \ldots, \hat{L}_{NS}^{N_{\text{iter}}}) + \sum_{j \epsilon S_k} \hat{L}_j^{N_{\text{iter}}}[\phi_j(y_k) - \epsilon_j - \bar{x}_{j,k-1}]$$

and

$$\bar{y}_{k-1} \le y_k \le \bar{y}_k$$

Program (AP$_k$) can be readily solved by plotting α_k vs. y_k, where the functional dependence of α_k on y_k is given by:

$$\alpha_k = \psi_k^S(y_k, \hat{L}_1^{N_{\text{iter}}}, \hat{L}_2^{N_{\text{iter}}}, \ldots, \hat{L}_{NS}^{N_{\text{iter}}}) - \psi_k^R(y_k) \tag{17}$$

for y_k ranging between $\bar{y}_{k-1}$ and $\bar{y}_k$. The solution of program AP$_k$ corresponds to the point where the plot of α_k vs. y_k has its lowest value. Let us denote this solution by:

$$\hat{\alpha}_k^{N_{\text{iter}}+1} \quad \text{and} \quad \hat{y}_k^{N_{\text{iter}}+1}.$$

(5) If the following criteria:

$$\hat{\alpha}_k^{N_{\text{iter}}+1} \ge 0 \quad k=1, 2, \ldots, K \tag{18}$$

are satisfied, terminate the procedure since the global solution has been identified. The optimal flow rates of the MSAs are given by $\hat{L}_1^{N_{\text{iter}}}, \hat{L}_2^{N_{\text{iter}}}, \ldots, \hat{L}_{NS}^{N_{\text{iter}}}$. In addition, a pinch location corresponds to any $\hat{y}_k^{N_{\text{iter}}+1}$ at which $\hat{\alpha}_k^{N_{\text{iter}}+1}$ is zero. If one or more of the K conditions described by Eq. 18 are not satisfied, proceed to step 6.

(6) Increase the counter N_{iter} by one and go to step 3.

By following this global optimization procedure to solve P1, one obtains the optimal values of the flow rates of all MSAs. One also identifies the location of the pinch point in the network, thereby decomposing the synthesis problem into two subnetworks, each referred to as SN_m ($m=1, 2$). Within each subnetwork, mass lost from the rich streams is identical to that gained by the lean streams. In general, n_p pinch points may be identified, thereby decomposing the network into n_p+1 subnetworks.

Minimization of the Number of Mass Exchangers

The first step in minimizing the number of mass exchangers is to create a composition-interval diagram "CID." On the CID, $NS+1$ vertical composition scales are established in a one-to-one correspondence via Eq. 2a. Next, each stream is represented as a vertical arrow whose tail and head correspond to its supply and target compositions, respectively. Horizontal lines are drawn at the heads and tails of the rich and the lean streams. In addition, a horizontal line is constructed at the location of the pinch. These horizontal lines create a maximum of $V=2NR+2NS$ composition intervals with $v=1$ being the uppermost composition interval and $v=V$ being the lowermost composition interval. The compositions at the lower end on the vth interval are designated by $\bar{y}_v, \bar{x}_{1,v}, \bar{x}_{2,v}, \ldots, \bar{x}_{NS,v}$. Let us denote the interval immediately above the pinch by $v=p$ and that immediately below the pinch as $v=p+1$. Hence, the compositions of the streams at the pinch point are designated as $\bar{y}_p, \bar{x}_{1,p}, \bar{x}_{2p}, \ldots, \bar{x}_{NS,p}$. It is important to check the convexity

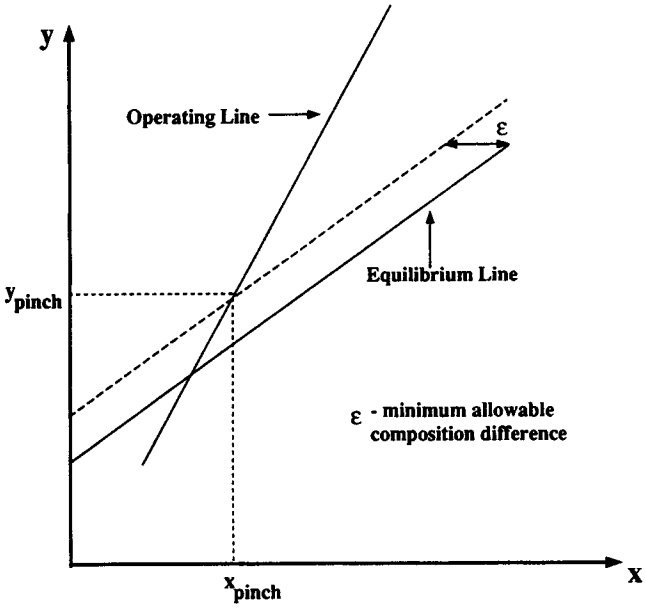

Figure 2a. Thermodynamic feasibility for linear equilibrium.

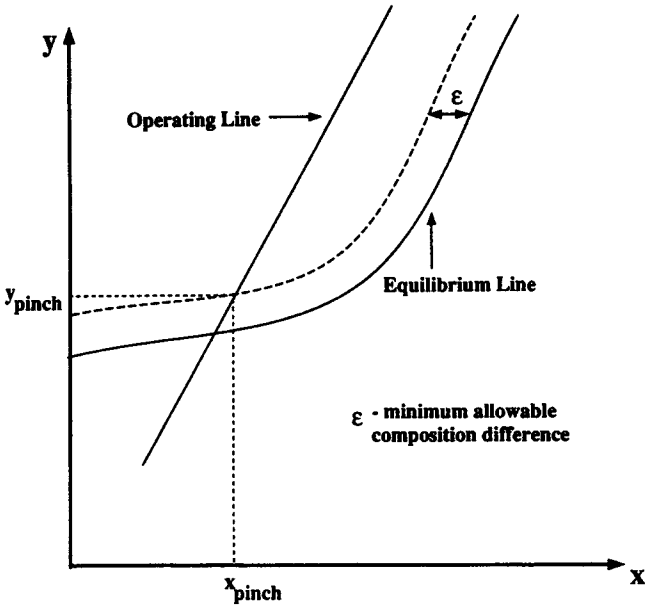

Figure 2b. Mass-exchange feasibility for convex equilibrium.

properties of the equilibrium function of each MSA at the pinch location.

If the equilibrium functions for all MSAs are linear or convex around the pinch point, it is impossible for any exchanger to straddle the pinch while maintaining the minimum acceptable driving force, ϵ_j, throughout the exchanger (see Figures 2a and 2b). In such cases, the mathematical formulation developed by El-Halwagi and Srinivas (1992) can be used to minimize the number of exchangers. Nonetheless, if at least one of the MSAs has a nonconvex equilibrium function around the pinch, it is possible for mass exchangers involving this MSA to straddle the pinch (Figure 2c). Since the formulation of El-Halwagi

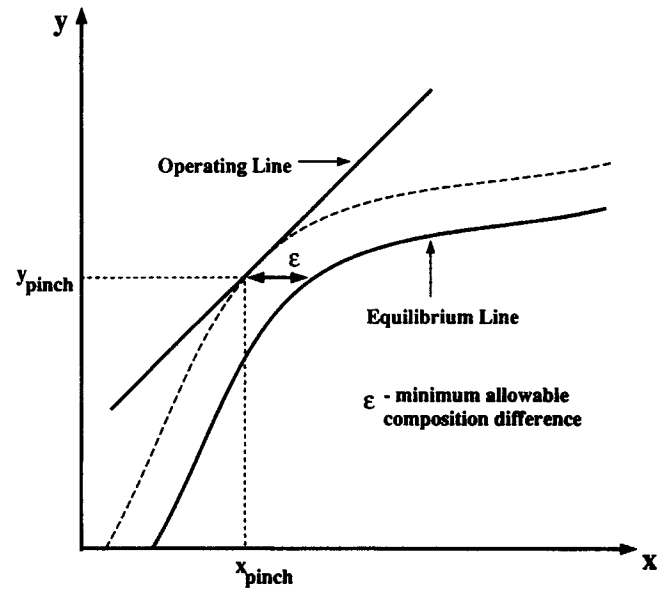

Figure 2c. Thermodynamic feasibility for nonconvex equilibrium.

and Srinivas (1992) was developed for linear/convex equilibria, it assumes that no mass exchanger can straddle the pinch; therefore, it is not applicable to the case when the equilibrium function around the pinch is nonconvex for at least one of the MSAs. In the sequel, we develop a systematic procedure to tackle this situation.

First, it is necessary to introduce the binary integer variables $E_{i,j,m}$ whose values become one (zero) when mass exchange between streams i and j in subnetwork m exists (vanishes). In order to do so we need to define the following subsets:

$$R_m = \{i \mid i \in R, \text{ stream } i \text{ exists in } SN_m\} \quad (19)$$

$$S_m = \{j \mid j \in S_m, \text{ stream } j \text{ exists in } SN_m\} \quad (20)$$

$$R_{m,v} = \{i \mid i \in R_m, \text{ stream } i \text{ exists in interval } \bar{v} \le v;\ \bar{v},\ v \in SN_m\} \quad (21)$$

$$S_{m,v} = \{j \mid j \in S_m, \text{ stream } j \text{ exists in interval } v \in SN_m\} \quad (22)$$

$$SP = \{j \mid j \in S, \text{ pinch point is surrounded by a nonconvex portion of the equilibrium of stream } j\} \quad (23)$$

$$RP = \{i \mid i \in R, \text{ stream } i \text{ straddles the pinch}\} \quad (24)$$

Clearly, the mass exchangeable between the ith and jth streams of subnetwork m cannot exceed the following upper bound:

$$U_{i,j,m} = \min\left[G_i \sum_{v \in SN_m} (\bar{y}_v - \bar{y}_{v+1}),\ L_j \sum_{v \in SN_m} (\bar{x}_{j,v} - \bar{x}_{j,v+1})\right] \quad (25)$$

where the summation for each stream is taken over the composition intervals within subnetwork m over which the stream exists.

In order to identify the existence/absence of a match between a rich stream i and a lean stream j in intervals p and $p+1$, we

need to define $W_{i,j,p}$ and $W_{i,j,p+1}$ to be the mass exchanged between rich stream i and lean stream j in intervals p and $p+1$, respectively.

We are now in a position to formulate the minimum number of mass-exchangers problem via the transshipment model, in which it is envisaged that mass is being transshipped from a set of sources (rich streams) to a set of sinks (MSAs) via intermediate warehouses (composition intervals), as:

$$\min E = \sum_{m=1,2} \sum_{i \in R_m} \sum_{j \in S_m} E_{i,j,m} - \sum_{i \in R_p} \sum_{j \in S_p} B_{i,j} \qquad \text{(P2)}$$

subject to:

Material Balance Constraints. The mass load entering any interval can be exchanged with the lean streams in that interval or may be passed down to a lower interval. This may be written as the following:

$$\delta_{i,v} - \delta_{i,v-1} + \sum_{j \in S_{m,v}} W_{i,j,v} = G_i(\bar{y}_v - \bar{y}_{v+1}) \quad i \in R_{m,v},\ v \in SN_m$$

where

$$\delta_{i,v} \geq 0 \quad i \in R_{m,v},\ v \in SN_m$$

Within any interval, the lean streams can receive only the mass that is available in that interval. Hence, we may write:

$$\sum_{i \in R_{m,v}} W_{i,j,v} = L_j(\bar{x}_{j,v} - \bar{x}_{j,v+1}) \quad j \in S_{m,v},\ v \in SN_m$$

Exchanger Counter Constraints. The following set of constraints identify the existence/absence of a match between rich stream i and lean stream j in subnetwork m. If any mass is exchanged between streams i and j and subnetwork m, there must exist an exchanger to achieve this. This is represented by the following set of constraints:

$$\sum_{v \in SN_m} W_{i,j,v} - U_{i,j,m} E_{i,j,m} \leq 0 \quad i \in R_m,\ j \in SN_m$$

where

$$W_{i,j,v} \geq 0 \quad i \in R_m,\ j \in S_m,\ v \in SN_m$$

and

$$E_{i,j,m} = 0,1 \quad \text{(binary integer variable)} \quad i \in R_m,\ j \in S_m,\quad m = 1,2$$

Straddling Exchanger Constraints. If there is an exchange of mass between the pair i and j where, $i \in$ RP, and j, $j \in$ SP, in intervals p and $p+1$, then there exists an exchanger between i and j that straddles the pinch. In such cases, $E_{i,j,1}$ and $E_{i,j,2}$ should be counted as one exchanger (rather than two). This can be accomplished by assigning the variable $B_{i,j}$ a value of one. The following constraints serve this purpose:

$$I_{i,j,p} * \eta \leq W_{i,j,p}$$

$$I_{i,j,p} * {}_{+1}\eta \leq W_{i,j,p+1}$$

$$I_{i,j,p} + I_{i,j,p+1} \geq 2\, B_{i,j}; \quad i \in \text{RP},\ j \in \text{SP}$$

$$I_{i,j,p} = 0,1 \quad \text{(binary integer variable)} \quad i \in \text{RP},\ j \in \text{SP}$$

$$I_{i,j,p+1} = 0,1 \quad \text{(binary integer variable)} \quad i \in \text{RP},\ j \in \text{SP}$$

$$B_{i,j} = 0,1 \quad \text{(binary integer variable)} \quad i \in \text{RP},\ j \in \text{SP}$$

In the above constraints, η is an arbitrary small number (for example, 10^{-5} kg/s). As can be inferred from these constraints, if $W_{i,j,p}$ and/or $W_{i,j,p+1}$ is zero, the value of $B_{i,j}$ is forced to be zero. On the other hand, if both $W_{ij,p}$ and $W_{i,j,p+1}$ are nonzeros, then $I_{i,j,p}$ and $I_{i,j,p+1}$ can take values of zero or one. Nonetheless, since the objective function attempts to maximize $B_{i,j}$, both $I_{i,j,p}$ and $I_{i,j,p+1}$ will assume a value of one so as to force the value of $B_{i,j}$ to be one. Therefore, when counting the exchangers $E_{i,j,1} + E_{i,j,2} - B_{i,j}$, we get $1 + 1 - 1 = 1$, confirming the fact that a pinch-straddling exchanger should be counted as one only.

The solution of the above mixed-integer linear program (MILP) identifies stream pairings, order of matches, stream splits, exchangeable loads and network configuration. Using this information, one can readily develop a complete design of the REAMEN. In order to demonstrate the usefulness of the developed systematic methodology, we now apply it to tackle a case study on the desulfurization of gaseous emissions from a coal liquefaction plant.

Case Study: Desulfurization of Gaseous Wastes From Coal Liquefaction

Coal liquefaction is one of the emerging technologies with great potential to supplement the world's future requirements of synthetic fuels. One way of liquefying coal is by converting it to methanol. In this process (Figure 3), coal is initially gasified to produce raw gas which is primarily a mixture of hydrogen, carbon monoxide and carbon dioxide (Jackson, 1982). This is then followed by the shift conversion process, wherein the carbon monoxide contained in the raw gas is converted in the presence of steam to carbon dioxide and hydrogen. This process also converts the sulfur present in coal to hydrogen sulfide. The shifted stream, $R1$, is fed to a desulfurization system to reduce its content of hydrogen sulfide to an environmentally and technically acceptable level. The desulfurized gas stream is then passed to a methanol-synthesis unit, wherein carbon dioxide and hydrogen react to produce methanol. Two

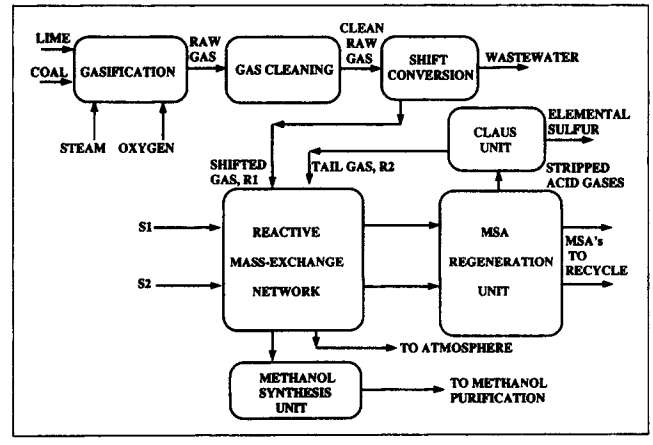

Figure 3. Simplified flowsheet of a coal-to-methanol plant.

Table 1. Data for the Waste Streams

Stream	Flow Rate of Inert kg/s	y_i^s (kg H_2S/kg Inert)	y_i^t (kg H_2S/kg Inert)
R_1	94.28	5.0×10^{-2}	5×10^{-3}
R_2	108.0	3.0×10^{-2}	5×10^{-3}

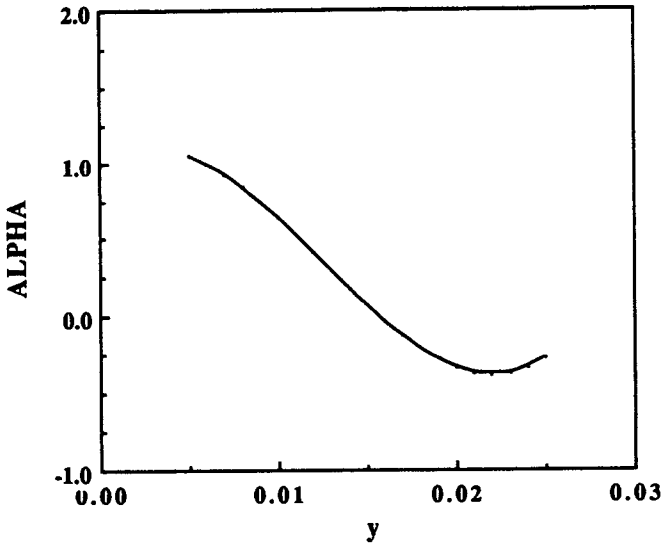

Figure 4a. Solution of AP_2 for the first iteration of the desulfurization case study.

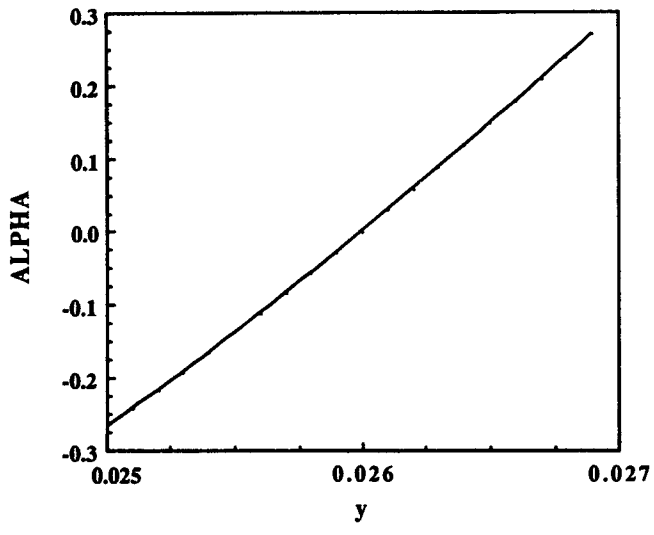

Figure 4b. Solution of AP_3 for the first iteration of the desulfurization case study.

Table 3. Equilibrium Data for Hydrogen Sulfide in the MSAs

MSA	Equilibrium $y=f_j(x_j)$	Equilibrium $x_j=\phi_j(y)$	ϵ_j	Ref.
S_1	$y=5.0x$	$x=0.2y$	5×10^{-3}	Kohl and Riesenfeld (1985)
S_2	$y=-197.19x^3+23.722x^2-0.3248x+0.0009928$	$x=6{,}046y^3-226.14y^2+4.081y+0.010869$	1×10^{-6}	Issacs (1980)

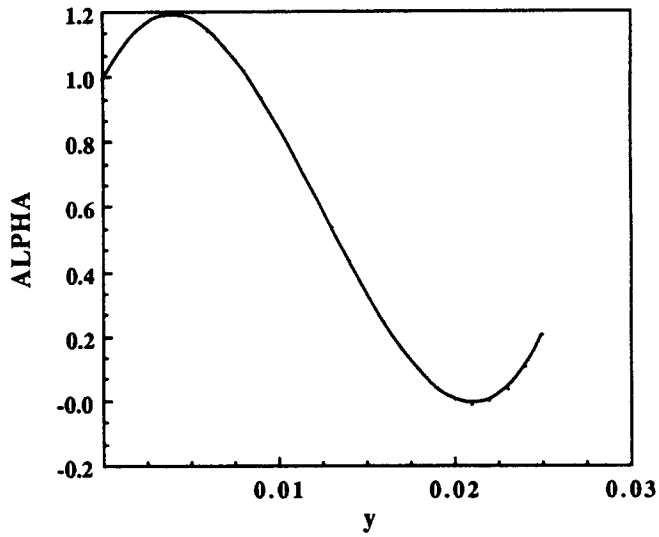

Figure 4c. Solution of AP_2 for the second iteration of the desulfurization case study.

MSAs can be employed for the removal of hydrogen sulfide. Methanol, $S1$, is a process MSA that exists within the plant. Monoethanolamine "MEA," $S2$, is an external MSA that can efficiently remove hydrogen sulfide. The solvents employed for desulfurization are subsequently regenerated for recycle. The stripped acid gas stream is sent to the Claus unit, whereby hydrogen sulfide is converted to elemental sulfur. The tail gas, $R2$, leaving the Claus unit is further treated for H_2S removal, prior to being discharged to the atmosphere.

It is desired to design a cost-effective desulfurization system to reduce the hydrogen sulfide content in the two rich gas streams ($R1$ and $R2$) using one or both of the two MSAs ($S1$ and $S2$). The stream data for this case study are given in Tables 1 and 2. The unit cost of $S2$, including makeup and regeneration is \$0.11/kg. The equilibrium data for the MSAs are given in Table 3. It is worth pointing out that the equilibrium function of $S2$ is nonconvex.

Table 2. Supply and Target Compositions for the MSAs

MSA	Description	x_j^s (kg H_2S/kg Solvent)	x_j^t (kg H_2S/kg Solvent)	L_j^c (kg/s Solvent)
S_1	Methanol	0.0	3.0×10^{-3}	900
S_2	50 wt. % MEA	1.113×10^{-2}	7.47×10^{-2}	∞

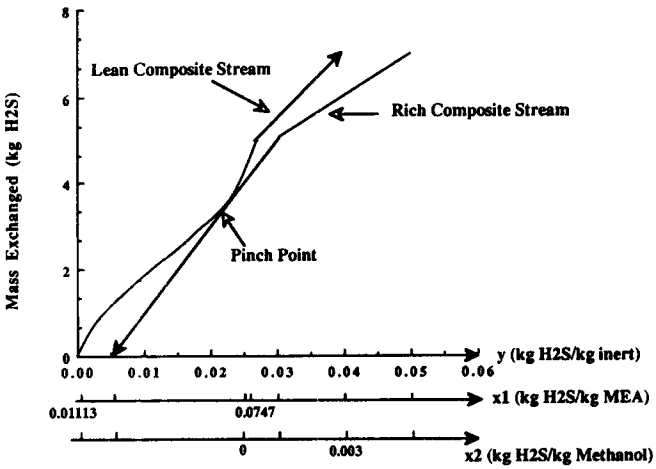

Figure 5. Pinch diagram for the desulfurization case study.

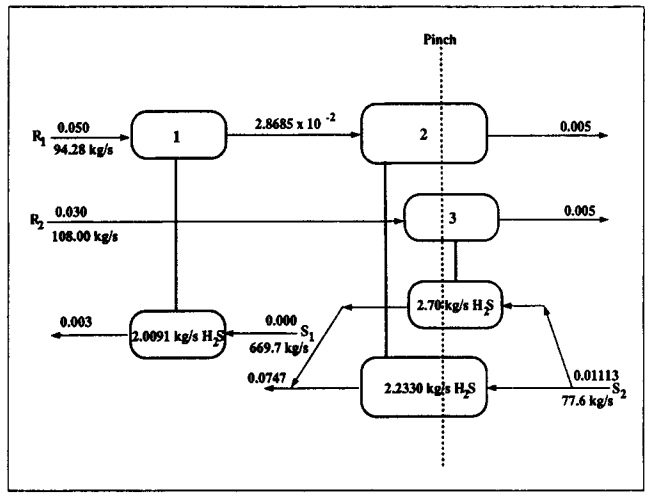

Figure 7. Optimal desulfurization REAMEN for the coal-to-methanol example.

In order to solve this case study, the proposed iterative algorithm is applied. The composition range was divided at inlets and outlets of streams to yield six composition intervals. Problem RP1 was initially solved for an arbitrary initial set of $\hat{y}_k^1$s for the six intervals {0.001, 0.01, 0.026, 0.028, 0.035, 0.045} for $k = 1, 2, \ldots, 6$ respectively. The flow rates of the MSAs corresponding to the solution of RP1 for the first iteration were obtained by using the software LINDO (Schrage, 1989) as $\hat{L}_1 = 855.9$ and $\hat{L}_2 = 68.8$ kg/s. Hence, problem AP_k was then solved for the six intervals. As shown in Figures 4a and 4b, it can be seen that thermodynamic feasibility for mass exchange is violated in intervals 2 and 3. All other intervals were feasible. In the second iteration, the solution of RP1 yielded $\hat{L}_1 = 674.7$ and $\hat{L}_2 = 77.4$ kg/s. At the end of the second iteration, thermodynamic feasibility was still not satisfied in the second interval (Figure 4c). The global solution for the above problem was found in the third iteration, and the optimum values for the flow rates of the two MSAs, *S*1 and *S*2, that one obtains are 669.7 kg/s and 77.6 kg/s respectively. The optimal solution has a reactive mass-exchange pinch point at 0.021 on the y scale.

Having solved the problem of minimizing the cost of MSAs for the above example, we can now plot the pinch diagram of the problem. As shown in Figure 5, it can be seen that the pinch does not correspond to the inlet composition of any stream in the problem. Further, it can also be seen that the location of the pinch is in the nonconvex portion of MEA. Next, the CID for the above problem was constructed (Figure 6). The MILP, P2, was then solved using LINDO. The optimal solution identified the minimum number of reactive mass-exchangers for the above problem, and necessary information regarding stream matches and stream splitting. The REAMEN for the above case study is shown in Figure 7. As indicated, the network features a minimum of three exchangers; two involving MEA and one using methanol. The two exchangers featuring MEA straddle the pinch.

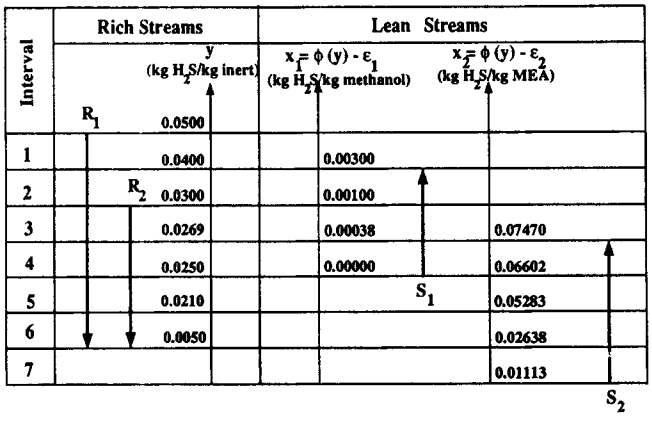

Figure 6. Composition-interval diagram for coal-to-methanol example.

Conclusion

We have developed a novel procedure for the synthesis of REAMENs featuring mass-separating agents that exhibit general nonlinear equilibrium distribution functions. A systematic two-stage procedure to synthesize REAMENs has been presented. First, it accomplishes the minimization of the cost of MSAs that is required to perform the specified mass-exchange task. A global optimization algorithm has been devised to identify optimal flow rates of the MSAs and pinch location. This step is followed by the minimization of the number of exchangers that are required subject to the minimum cost of MSAs. The proposed procedure accounts for cases when exchangers can straddle the pinch. A case study on desulfurizing gaseous emissions from a coal-to-methanol plant has been solved to demonstrate the applicability of the proposed procedure.

Acknowledgment

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Notation

$B_{i,j}$ = binary variable to account for pinch-straddling matches
c_j = unit cost of the jth MSA, \$/kg
f_j = equilibrium distribution function for the undesirable species in the jth MSA, as defined in Eq. 1
G_i = flow rate of the ith rich stream, kg/s

i = index for rich streams
$I_{i,j,p}$ = binary variable for a match between the pair i and j in interval p
$I_{i,j,p+1}$ = binary variable for a match between the pair i and j in interval $p+1$
j = index for lean streams
k = index for composition intervals of a pinch diagram
K = total number of composition intervals
L_j = flow rate of the jth MSA, kg/s
L_j^c = upper bound on the flow rate of the jth MSA, kg/s
m = index for subnetworks
n_p = number of mass-exchange pinch points in the problem
NR = number of rich streams in set R
NS = number of MSAs in set S
N_{iter} = number of iterations for solving the problem of minimizing cost of MSAs
r = index for iterations for solving the problem of minimizing cost of MSAs
R = set of waste streams
R_i = ith rich stream
R_k = set of rich streams in interval k, as defined in Eq. 3a
R_m = set of rich streams in subnetwork m, as defined in Eq. 19
$R_{m,v}$ = set of rich streams existing in interval v of subnetwork m, as defined in Eq. 21
RP = set of rich streams straddling the pinch, as defined in Eq. 24
S = set of MSAs
S_j = jth lean stream
S_k = set of lean streams in interval k, as defined in Eq. 3b
S_m = set of lean streams in subnetwork m, as defined in Eq. 20
$S_{m,v}$ = set of lean streams existing in interval v of subnetwork m, as defined in Eq. 22
SP = set of lean streams straddling the pinch, as defined in Eq. 23
SN_m = subnetwork m
$U_{i,j,m}$ = upper bound on the load that can be exchanged between streams i and j in subnetwork m, as defined in Eq. 25
v = index for composition intervals in the CID
V = total number of composition intervals in the CID
$W_{i,j,p}$ = load exchanged between streams i and j in interval p, kg/s
$W_{i,j,p+1}$ = load exchanged between streams i and j in interval $p+1$, kg/s
$W_{i,j,v}$ = load exchanged between streams i and j in interval v, kg/s
x_j = composition of the undesirable component in the jth lean stream, kg transferable species/kg jth MSA
x_j^s = supply composition of the undesirable component in the jth lean stream, kg transferable species/kg jth MSA
x_j^t = target composition of the undesirable component in the jth lean stream, kg transferable species/kg jth MSA
x_j^* = equilibrium composition of the undesirable component in the jth lean stream, kg transferable species/kg jth MSA
y = composition of the undesirable component in any rich stream, kg transferable species/kg rich stream
y_i^s = supply composition of the undesirable component in the ith rich stream, kg transferable species/kg rich stream
y_i^t = target composition of the undesirable component in the ith rich stream, kg transferable species/kg rich stream
y^* = equilibrium composition of the undesirable component in the ith rich stream, kg transferable species/kg rich stream

Greek letters

α_k = vertical distance between the lean- and the rich-composite streams at some composition y_k, kg/s
$\delta_{i,v}$ = residual load leaving interval v, kg/s
ϵ_j = minimum allowable composition difference for the jth MSA
η = arbitrary small number
ϕ_j = inverse equilibrium function for the jth MSA, as defined by Eq. 2b
ψ = cumulative mass exchanged by the composite stream, kg/s

Subscripts

i = index for waste streams belonging to set R
j = index for MSAs belonging to set S
k = within the kth composition interval
p = composition interval immediately above the pinch
v = index for the composition intervals of a CID

Superscripts

R = rich
s = supply composition
S = lean
t = target composition
$*$ = equilibrium composition

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