Simultaneous Synthesis of Mass-Exchange and Regeneration Networks

A systematic procedure is developed for the simultaneous synthesis of primary transfer mass-exchange networks and their associated mass-exchange regeneration networks. The purpose of the primary transfer network is to preferentially transfer certain species from a set of rich streams to a set of lean streams. The regeneration network aims at regenerating any recyclable lean stream. The proposed procedure deals with the problem in two stages. In the first stage, a mixed-integer nonlinear program is solved to minimize the cost of mass-separating and regenerating agents. The solution of this program provides the location of the pinch points as well as the optimal flow rates of all the lean and the regenerative streams *without any prior commitment to the network structure.* In the second stage, a mixed-integer linear program is solved to minimize the number of exchangers in both networks. An example problem with industrial relevance is solved to elucidate the merits offered by the devised synthesis procedure.

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Introduction

In most chemical process industries, economic, technical, and environmental considerations often necessitate mass exchange. Mass-exchange operations are diverse and span a wide range of applications, such as raw material preparation, product purification and finishing, reuse of mass-separating agents, and recovery of valuable species. Another important area involving mass-exchange processes is waste minimization. The growing awareness of the consequences of discharging effluents into natural resources has led to corrective measures, both voluntary and legislated. Recently, added incentives and pressures to recover and recycle hazardous species from industrial effluents have come to bear and have resulted in the utilization of recycle/reuse networks for hazardous waste minimization. These networks typically involve the transfer of certain species from rich streams to lean streams. The problem of matching pairs of rich and lean streams is inherently combinatorial. Consequently, it is important for the designer to have a systematic tool that reduces the problem dimensionality to a manageable size and provides cost-effective networks. Motivated by this need, we have recently introduced the notion of mass-exchange network (MEN) synthesis (El-Halwagi and Manousiouthakis, 1989).

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 species from a set of rich streams to a set of lean streams. By a mass exchanger we mean any countercurrent direct-contact mass-transfer unit operation that employs a mass-separating agent (MSA) for the selective transfer of certain solutes. The lean streams may exist at the plant site at a reduced cost (process MSAs) or may be purchased (external MSAs) to supplement the assigned separation task. Examples of mass exchange operations are solvent extraction, lixiviation, absorption, adsorption, stripping, and ion exchange. In our previous work (El-Halwagi and Manousiouthakis, 1989) we proposed a targeting procedure that divides the problem into two stages. In the first stage, the minimum cost of MSAs is identified without prior commitment to the network structure. Next, the fixed cost is minimized by generating a network that features the smallest number of exchangers subject to the minimum cost of MSAs. With this systematic procedure, even complex industrial problems can be taken up without difficulty.

Depending on the subsequent operations associated with the MSAs leaving the network, one may classify the lean streams into two categories: once-through MSAs and regenerable MSAs. Once-through MSAs are typically encountered either when there is no economic nor environmental incentive to regenerate the lean streams leaving the MEN (throwaway processes) or

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when the effluent MSAs become valuable feedstocks upon acquiring the transferrable species. With regenerable MSAs, on the other hand, there is a strong economic and/or environmental motivation to recover solutes and/or regenerate the MSAs for recycle purposes. While our previous work has been confined to the problem of synthesizing MENs that employ only once-through MSAs, the present work deals with the situations in which both once-through and regenerable MSAs are involved in the MEN.

In this paper we address the problem of simultaneously synthesizing primary and secondary (regeneration) mass-exchange networks. We denote as primary the network that involves the exchange among the rich streams and the lean streams, whereas we denote as secondary or regeneration the network that involves the exchange among the regenerable MSAs and the regenerating agents. Since these two networks interact with one another, through the regenerable MSAs, their synthesis is pursued simultaneously. Indeed, a sequential synthesis procedure may prejudice the design of one of the networks, thus preventing the establishment of design targets for the overall system. In developing our simultaneous synthesis methodology, we first formulate a mixed-integer nonlinear program whose solution yields the total minimum cost of the lean streams in both networks. This target is identified without any prior commitment to the structure of the two MENs and is based on thermodynamic considerations. Next, we formulate a mixed-integer linear program whose objective is to minimize the total number of mass exchangers in a primary/secondary network pair that features minimum operating cost.

Problem Description

Problem statement

The problem of simultaneously synthesizing a primary-transfer MEN and its regeneration MEN, Figure 1, can be outlined as follows: Given

(i) a set

$R = \{i | i = 1, N_R\}$ of rich process streams

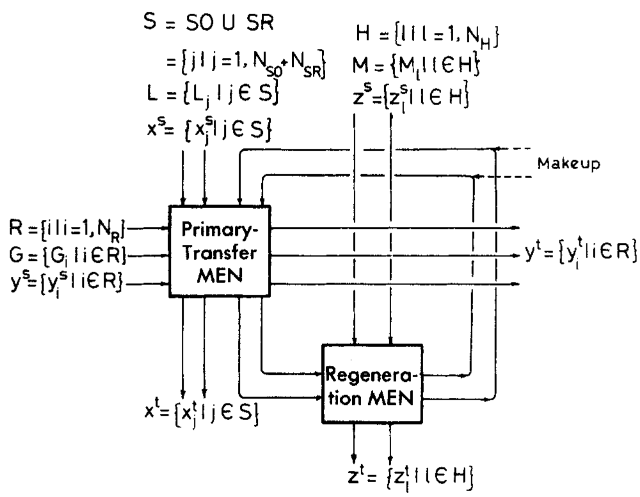

Figure 1. Primary transfer and regeneration mass-exchange networks.

(ii) a set

$S = \{j | j = 1, N_{SO} + N_{SR}\}$ of lean streams, which consists of

a subset

$SO = \{j | j = 1, N_{SO}\}$ of once-through lean streams (once-through MSAs)

and a subset

$SR = \{j | j = N_{SO+1}, N_{SO} + N_{SR}\}$ of regenerable (recyclable) lean streams (regenerable MSAs)

(iii) a set

$H = \{l | l = 1, N_H\}$ of regenerants (regenerative MSAs)

synthesize in a cost-effective manner a primary transfer MEN that can transfer certain species from the rich streams to the lean streams and a regeneration MEN that can regenerate the recyclable lean streams.

Problem constraints

Each rich stream has a given mass flow rate G_i and ought to be brought from a known supply composition y_i^s to a specified target composition y_i^t. Similarly, each once-through lean stream has a given supply composition x_j^s and a specified target composition x_j^t. The mass flow rates of all the lean streams are unknown but are bounded by the following availability constraint

$$L_j \leq L_j^c \qquad j \in S \tag{1}$$

The supply and target compositions of every regenerative MSA, z_l^s and z_l^t, are also given. The mass flow rate of each regenerant is unknown but is bounded by the following resource-availability constraint

$$M_l \leq M_l^c \qquad l \in H \tag{2}$$

The compositions of the recyclable MSAs are unknown. However, the composition of every recyclable MSA is bounded by the following constraints

$$x_j^l \leq x_j^s \leq x_j^t \leq x_j^c \qquad j \in SR \tag{3}$$

The nature of such constraints may be physical (e.g., maximum solubility of solute in solvent) or technical (to avoid excessive corrosion, viscosity, or fouling) or environmental (as set by the environmental protection regulations).

The objective is to simultaneously synthesize both the primary transfer and the regeneration MENs that can accomplish the assigned exchange duties at minimum venture cost. This task involves the identification of the optimal flow rates of all the lean streams as well as the regenerating agents, the supply and target compositions for each recyclable lean stream, and the structure of both MENs.

Problem Characteristics

In developing the simultaneous MEN synthesis procedure, we employ several properties of the once-through MEN synthesis problem. It therefore seems appropriate to summarize here these important problem characteristics. First, let us consider the equilibrium relation governing the distribution of the key component between a rich stream and the jth lean stream to be given by

$$y = m_j x_j + b_j \qquad j = 1, 2, \ldots, N_{SO} + N_{SR} \tag{4}$$

for the primary network, and the equilibrium relation for the system involving a regenerable lean stream and the lth regenerating agent to be given by

$$x = m_l' z_l + b_l' \qquad l = 1, 2, \ldots, N_H \tag{5}$$

for the secondary network. In the sequel, we shall examine the problem characteristics associated only with the primary transfer MEN. Then, one can readily extend these properties to the regeneration network by considering the regenerable lean streams and the regenerating agents to play the roles of the rich and the lean streams, respectively. As indicated by Eq. 4, the maximum theoretically attainable value of x_j operating with some given y_i is

$$x_j^* = \frac{y_i - b_j}{m_j} \tag{6}$$

Clearly, to achieve this equilibrium condition, one must have an infinitely large mass exchanger. Thus, one ought to assign a minimum allowable composition difference between the equilibrium and the operating compositions of a lean stream, $\epsilon_{i,j}$. In other words, the maximum practically feasible composition of the jth lean stream is expressed as

$$x_j^{max} = \frac{y_i - b_j}{m_j} - \epsilon_{i,j} \tag{7}$$

Equation 7 is used to create a correspondence among the various composition scales involved in the problem. For simplicity of the following analysis, a single value for $\epsilon_{i,j}$ is used in all composition scales. Nonetheless, one can readily employ a stream-dependent minimum allowable composition difference without altering the basic structure of this analysis. Since the equilibrium relations are considered to be functions of the solute–solvent system only, one may use a single key component scale, y, for all the rich streams. Then, based on Eq. 7, one can create the composition interval diagram (CID) consisting of a series of composition intervals that correspond to the supply or target composition of each stream. One of the principal uses of the CID is in identifying the most thermodynamically constrained region of design, that is, the pinch point. This is achieved for the case of fixed supply and target compositions of all lean streams by solving a simple linear program that minimizes the cost of MSAs (El-Halwagi and Manousiouthakis, 1990). If any mass is transferred across the pinch, this will result in the penalty of incurring more than the minimum cost of MSAs. Therefore, the pinch point decomposes the synthesis problem into two subnetworks: a rich-end subnetwork above the pinch, and a lean-end subnetwork below the pinch. Generally, when n_p pinch points exist, the synthesis problem can be decomposed into $n_p + 1$ subnetworks.

It is beneficial to examine several properties provided by the graphical representation of the problem. For example, let us consider a problem of synthesizing a MEN with two rich streams and two once-through lean streams. Given are the inlet and outlet compositions for all the rich and the lean streams, the flow rates of the rich streams, and the unit cost associated with each lean stream. As depicted by Figure 2a, one can employ Eq. 7 to establish the correspondence among the composition scales y, x_1, and x_2. Next, the mass transferrable by every stream is plotted vs. the composition as a straight line extending between the supply and the target compositions with a slope equal to the flow rate of the relevant stream. Since the flow rates of the lean streams are unknown, they are plotted as dotted lines to indicate that their slopes are unknown. Clearly, the vertical scale is only relative and, thus, any stream can be slid upward or downward on this diagram. The problem of determining the minimum cost of MSAs involves evaluating the lean-stream flow rates and locating the pinch points in both networks. This task can be accomplished easily by solving a simple transshipment linear program whose objective function is the cost of MSAs and whose constraints are overall material balance equations around each composition interval (El-Halwagi and Manousiouthakis, 1990). The obtained solution can be represented graphically by plotting the composite rich and the composite lean streams, which are simply the individual streams merged into a composite stream via linear superposition. If both composite streams are moved until they touch at the pinch point, Figure 2B, one can notice the following properties:

1. If one is to locate the pinch graphically, one should consider as potential pinch candidates only those corner points on the composite streams that correspond to the inlets of any rich or lean stream, excluding the inlet points that fall outside the composition range shared by both composite streams. This property is inferred by noting that the two composite streams can touch only at a corner point where one composite curve approaches and then breaks away from the other curve. Therefore, in Figure 2b the pinch point candidates are the inlet points of S_2 and R_2. We shall refer to the set of pinch point candidates in the primary transfer MEN by P. An analogous observation was noted in the context of locating thermal pinch points in heat-exchange network synthesis (Grimes, 1980; Cerda et al., 1983; Duran and Grossmann, 1986).

2. Clearly, a total material balance for the network (total mass lost by the rich streams in the network equals total mass gained by the lean streams in the network) must always be realized. Furthermore, since the realization of the minimum cost of MSAs requires that no mass be transferred across the pinch, it can be shown without difficulty that the pinch decomposes the problem into two independent portions, a rich end and a lean

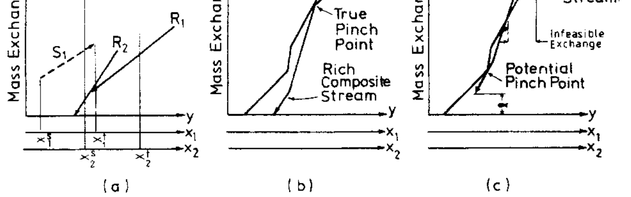

Figure 2. Geometrical properties of the minimum utility problem.

end. The material balance for each portion (mass gained by lean streams equals mass lost by rich streams) is satisfied, Figure 2b.

3. As demonstrated by Figure 2b, thermodynamic feasibility of mass exchange is insured if and only if the lean composite stream lies above the rich composite stream at every composition level, with both streams being touched only at the true pinch point.

4. If both composite streams are to be touched at any pinch point candidate other than the true pinch point, Figure 2c, the rich composite stream must be slid upward a vertical distance α until it touches the lean composite stream at that pinch point candidate. Recalling property 3, above, one can readily notice that such an exchange situation is thermodynamically infeasible (since some portions of the lean composite stream lie below the corresponding portions of the rich composite stream at the same composition range) and that the following expressions hold true:

$$\begin{matrix}\text{Mass lost by the} \\ \text{rich streams above} \\ \text{the pinch point} \\ \text{candidate}\end{matrix} - \begin{matrix}\text{mass gained by} \\ \text{the lean streams} \\ \text{above the pinch} \\ \text{point candidate}\end{matrix} = \alpha \quad \alpha \geq 0 \tag{8a}$$

and

$$\begin{matrix}\text{Mass gained by the} \\ \text{lean streams below} \\ \text{the pinch point} \\ \text{candidate}\end{matrix} - \begin{matrix}\text{mass lost by the} \\ \text{rich streams below} \\ \text{the pinch point} \\ \text{candidate}\end{matrix} = \alpha \quad \alpha \geq 0 \tag{8b}$$

with α vanishing only at the true pinch point. In other words,

$$\begin{matrix}\text{Mass lost by the} \\ \text{rich streams above} \\ \text{the pinch point} \\ \text{candidate}\end{matrix} - \begin{matrix}\text{mass gained by the} \\ \text{lean streams above} \\ \text{the pinch} \\ \text{point candidate}\end{matrix} \geq 0 \quad p \in P \tag{9a}$$

and

$$\begin{matrix}\text{Mass lost by the} \\ \text{rich streams below} \\ \text{the pinch point} \\ \text{candidate}\end{matrix} - \begin{matrix}\text{mass gained by the} \\ \text{lean streams below} \\ \text{the pinch point} \\ \text{candidate}\end{matrix} \leq 0 \quad p \in P \tag{9b}$$

with the equality applying in Eqs. 9a and 9b when the pinch point candidate is the true pinch point. Not only do Eqs. 9a and 9b characterize the true pinch point, they also provide explicit criteria for thermodynamic feasibility of exchange. This is attributed to the previous observation that if the two composite streams are brought in contact at any pinch point candidate other than the true pinch point, the resulting exchange is thermodynamically infeasible. Since the total material balance for the network must always hold, one can eliminate either Eq. 9a or Eq. 9b as a feasibility criterion in favor of the total material balance. Throughout this paper we select Eq. 9b and the total material balance equation to identify the true pinch point and to insure thermodynamic feasibility.

Design Targets

It is worth pointing out that the problem of simultaneously synthesizing a primary transfer MEN and a regeneration MEN is a combinatorial one. Therefore, it is desirable to develop a targeting procedure that decomposes the problem to subproblems of manageable size. Based upon thermodynamic and economic properties of the problem, the proposed procedure establishes the following targets ahead of design:

1. *Minimum Cost of MSAs and Regenerating Agents.* Thermodynamics may limit the extent of mass exchanged between the various pairs of streams involved in the problem. Therefore, one can utilize these thermodynamic constraints to help identify the minimum cost of MSAs and regenerating agents considered together. Any design that attains the minimum cost of MSAs and regenerating agents will be denoted as a minimum-utility design.

2. *Minimum Number of Mass Exchange Units.* Since the cost of each mass exchanger is usually a concave function of the unit size, this objective attempts to minimize indirectly the fixed cost of the network. Normally, the minimum number of units in the primary-transfer MEN is related to the total number of streams by the following expression:

$$\begin{matrix}\text{Minimum number of} \\ \text{exchangers in the} \\ \text{primary transfer MEN}\end{matrix} = N_R + N_S - N_i \tag{10}$$

where N_i is the number of independent synthesis subproblems into which the primary MEN synthesis problem can be subdivided. Similarly, the fewest number of mass exchangers in the regeneration network is given by:

$$\begin{matrix}\text{Minimum number of} \\ \text{exchangers in the} \\ \text{regeneration network}\end{matrix} = N_{SR} + N_H - N_i' \tag{11}$$

where again N_i' is the number of independent subproblems into which the regeneration problem can be subdivided.

With the foregoing insights and targets in mind, we can now present our proposed methodology for the simultaneous synthesis of primary transfer and regeneration networks.

Design Procedure

For convenience in representation throughout this paper, we employ the same framework discussed in our previous paper (El-Halwagi and Manousiouthakis, 1989). For all material balance purposes, we consider the flow rate of any regenerable lean stream to remain constant through both MENs. This assumption applies when moderate changes in compositions are involved, or when the transfer in one direction is balanced by a countertransport from the other phase. Nonetheless, if the flow rate variations are significant, the procedure can readily be adapted to deal with mass flow rates of the nontransferrable (inert) components instead of mass flow rates of the whole streams, and mass ratios (kg key component/kg inert components) instead of mass fractions. Any considerable change in the flow rate of a regenerable MSA ought to be substituted with makeup. Clearly, in this situation the concentration of the recycled MSA leaving the regeneration network will not be equal to that fed to the primary transfer MEN. Nonetheless, a simple material balance equation around the mixing point of the makeup and the regenerated MSA provides the concentration of the stream entering the primary transfer MEN. It is worth pointing out that even though the amount of MSA makeup may be negligible for material balance purposes, it will always be accounted for during the evaluation of the cost of the regenerable MSAs.

Minimum utility cost problem

This problem aims at minimizing the costs of the MSAs and the regeneration agents. This requires the evaluation of the optimum flow rates of all the lean streams and the regenerating agents, the identification of the optimal supply and target compositions for all the regenerable MSAs, and the location of pinch points within both MENs. As previously discussed, since the problem of locating the pinch and insuring thermodynamic feasibility entails incorporating material balance constraints below each pinch point candidate, one ought to have explicit expressions for the exchange loads of the rich, the lean, and the regenerating streams below each potential pinch point. It is, therefore, convenient to introduce the following binary integer variables:

$$\lambda_{i,p}^{t} = \begin{cases} 1 \text{ if } y_i^t < y^p & i \in R \\ 0 \text{ if } y_i^t \geq y^p & p \in P \end{cases} \quad (12)$$

$$\lambda_{i,p}^{s} = \begin{cases} 1 \text{ if } y_i^s < y^p & i \in R \\ 0 \text{ if } y_i^s \geq y^p & p \in P \end{cases} \quad (13)$$

$$\eta_{j,p}^{t} = \begin{cases} 1 \text{ if } x_j^t < x_j^p & j \in S \\ 0 \text{ if } x_j^t \geq x_j^p & p \in P \end{cases} \quad (14)$$

$$\eta_{j,p}^{s} = \begin{cases} 1 \text{ if } x_j^s < x_j^p & j \in S \\ 0 \text{ if } x_j^s \geq x_j^p & p \in P \end{cases} \quad (15)$$

where y^p and x_j^p are the equivalent compositions of the rich streams and the jth lean stream at the pinch point candidate $p \in P$ in the primary transfer network. Therefore, we have the following expressions:

$$\begin{array}{c}\text{Mass lost by}\\ \text{rich stream } i\\ \text{below a potential pinch}\\ \text{point in the primary}\\ \text{transfer MEN}\end{array} = G_i\{\lambda_{i,p}^t(y^p - y_i^t) - \lambda_{i,p}^s(y^p - y_i^s)\} \qquad \begin{array}{c} i \in R \\ p \in P \end{array} \quad (16)$$

and

$$\begin{array}{c}\text{Mass gained by lean}\\ \text{stream } j \text{ below a}\\ \text{potential pinch point}\\ \text{in the primary}\\ \text{transfer MEN}\end{array} = L_j\{\eta_j^s(x_j^p - x_j^s) - \eta_j^t(x_j^p - x_j^t)\} \qquad \begin{array}{c} j \in S \\ p \in P \end{array} \quad (17)$$

The above expressions parametrize the exchange loads below the pinch point candidates. To demonstrate their usefulness let us consider all the possible locations of rich stream i with respect to the pinch and examine the validity of Eq. 16.

1. When rich stream i lies completely above a potential pinch point p, then according to Eqs. 12 and 13 we have $\lambda_{i,p}^t = \lambda_{i,p}^s = 0$ and the ith rich stream load below the potential pinch point is zero, as expected.

2. When rich stream i exists completely below the potential pinch point, then as inferred from Eqs. 12 and 13, the value of each $\lambda_{i,p}^t$ and $\lambda_{i,p}^s$ is unity and the ith rich load below the potential pinch point is

$$G_i\{(y_p - y_i^t) - (y^p - y_i^s)\} = G_i(y_i^s - y_i^t)$$

which is the proper expression.

1. When the ith rich stream straddles the potential pinch point ($y_i^s > y^p$ and $y_i^t < y^p$), then as indicated by Eqs. 12 and 13 we get $\lambda_{i,p}^s = 0$ and $\lambda_{i,p}^t = 1$. Thus, the ith rich stream load below the potential pinch point is

$$G_i[(y^p - y_i^t) - 0] = G_i(y^p - y_i^t)$$

which represents the correct expression.

It is worth mentioning that instead of employing the integer variables in Eqs. 16 and 17, one may follow an alternate approach by utilizing max operators to parametrize the stream locations in a similar fashion to the parametric representation of stream inlet and outlet temperatures that Duran and Grossmann (1986) employed in the context of heat-exchange network synthesis. Nonetheless, such an alternate formulation causes nondifferentiability in the mathematical program and thus requires a special nonsmooth optimization algorithm to solve it.

In a similar manner to Eqs. 12 and 13 one may introduce the following binary integer variables for the regeneration network:

$$\psi_{j,q}^{s} = \begin{cases} 1 \text{ if } x_j^s < x^q & j \in SR \\ 0 \text{ if } x_j^s \geq x^q & q \in Q \end{cases} \quad (18)$$

$$\psi_{j,q}^{t} = \begin{cases} 1 \text{ if } x_j^t < x^q & j \in SR \\ 0 \text{ if } x_j^t \geq x^q & q \in Q \end{cases} \quad (19)$$

$$\phi_{l,q}^{s} = \begin{cases} 1 \text{ if } z_l^s < z_l^q & l \in H \\ 0 \text{ if } z_l^s \geq z_l^q & q \in Q \end{cases} \quad (20)$$

$$\phi_{l,q}^{t} = \begin{cases} 1 \text{ if } z_l^t < z_l^q & l \in H \\ 0 \text{ if } z_l^t \geq z_l^q & q \in Q \end{cases} \quad (21)$$

where x^q and z_l^q are the equivalent compositions of the regenerable lean streams and the lth regenerating agent at the pinch point candidate $q \in Q$ in the regeneration network. Hence, one can write the following relations:

$$\begin{array}{c}\text{Mass lost by the}\\ j\text{th regenerable MSA}\\ \text{below a potential}\\ \text{pinch point } q\\ \text{in the regeneration MEN}\end{array} = L_j\{\psi_{j,q}^s(x^q - x_j^s) - \psi_{j,q}^t(x^q - x_j^t)\} \qquad \begin{array}{c} j \in SR \\ q \in Q \end{array} \quad (22)$$

and

$$\begin{array}{c}\text{Mass gained by}\\ \text{regenerating agent } l\\ \text{below a potential pinch}\\ \text{point } q \text{ in the}\\ \text{regeneration MEN}\end{array} = M_l\{\phi^s_{l,q}(z^q_l - z^s_l) - \phi^t_l(z^q_l - z^t_l)\} \qquad \begin{array}{c} l \in H \\ q \in Q \end{array} \quad (23)$$

It should be noted that the compositions of each regenerable lean stream must be within a certain range dictated by thermodynamics. For instance, the supply composition of any regenerable lean stream must be larger than that in equilibrium with the supply composition of the regenerating agent with the smallest supply composition, that is,

$$x^s_j \geq x^{s,min}_j = m'_l(z^{s,min}_l + \epsilon'_{j,l}) + b'_j \quad (24)$$

where ϵ'_{jl} is the minimum allowable composition difference between lean stream j and regenerating agent l and

$$z^{s,min}_l = \min_l \{z^s_l, z^s_2, \ldots, z^s_{N_H}\} \quad (25)$$

Similarly, one can bound the target compositions of the jth lean stream by noting that it cannot be higher than that in equilibrium with the highest supply composition of rich streams, that is,

$$x^t_j \leq x^{t,max}_j = \left(\frac{y^{s,max}_i - b_j}{m_j}\right) - \epsilon_{i,j} \quad (26)$$

where

$$y^{s,max}_i = \max_i \{y^s_1, y^s_2, \ldots, y^s_{N_R}\} \quad (27)$$

Having established the parametric representation of all the exchange loads below the pinch point candidates and the feasible space for each regenerable lean stream, we are now in a position to present our mathematical formulation of the minimum utility cost problem as follows:

$$\min \sum_{j\in S} c_j L_j + \sum_{l\in H} c'_l M_l \quad (P1)$$

subject to

$$\sum_{i\in R} G_i(y^s_i - y^t_i) - \sum_{j\in S} L_j(x^t_j - x^s_j) = 0$$

$$\sum_{i\in R} G_i\{\lambda^t_{i,p}(y^p - y^t_i) - \lambda^s_{i,p}(y^p - y^s_i)\} - \sum_{j\in S} L_j\{\eta^s_{j,p}(x^p_j - x^s_j) - \eta^t_{j,p}(x^p_j - x^t_j)\} \leq 0 \qquad \forall\, p \in P$$

$$\sum_{j\in SR} L_j(x^t_j - x^s_j) - \sum_{l\in H} M_l(z^t_l - z^s_l) = 0$$

$$\sum_{j\in SR} L_j\{\psi^s_{j,q}(x^q - x^s_j) - \psi^t_{j,q}(x^q - x^t_j)\} - \sum_{l\in H} M_l\{\phi^s_{l,q}(z^q_l - z^s_l) - \phi^t_{l,q}(z^q_l - z^t_l)\} \leq 0 \qquad \forall\, q \in Q$$

$$0 \leq L_j \leq L^c_j \qquad j \in S$$

$$0 \leq M_l \leq M^c_l \qquad l \in H$$

$$x^{s,min}_j \leq x^s_j < x^t_j \leq x^{t,max}_j \qquad j \in SR$$

$$(2\lambda^t_{i,p} - 1)(y^p - y^t_i) \geq 0 \qquad i \in R, p \in P$$

$$(2\lambda^s_{i,p} - 1)(y^p - y^s_i) \geq 0 \qquad i \in R, p \in P$$

$$(2\eta^t_{j,p} - 1)(x^p_j - x^t_j) \geq 0 \qquad j \in S, p \in P$$

$$(2\eta^s_{j,p} - 1)(x^p_j - x^s_j) \geq 0 \qquad j \in S, p \in P$$

$$(2\psi^s_{j,q} - 1)(x^q - x^s_j) \geq 0 \qquad j \in SR, q \in Q$$

$$(2\psi^t_{j,q} - 1)(x^q - x^t_j) \geq 0 \qquad j \in SR, q \in Q$$

$$(2\phi^s_{l,q} - 1)(z^q_l - z^s_l) \geq 0 \qquad l \in H, q \in Q$$

$$(2\phi^t_{l,q} - 1)(z^q_l - z^t_l) \geq 0 \qquad l \in H, q \in Q$$

$$\lambda^s_{i,p} = 0, 1 \qquad i \in R$$

$$\lambda^t_{i,p} = 0, 1 \qquad i \in R$$

$$\eta^s_{j,p} = 0, 1 \qquad j \in S$$

$$\eta^t_{j,p} = 0, 1 \qquad j \in S$$

$$\psi^s_{j,q} = 0, 1 \qquad j \in SR$$

$$\psi^t_{j,q} = 0, 1 \qquad j \in SR$$

$$\phi^s_{l,q} = 0, 1 \qquad l \in H$$

$$\phi^t_{l,q} = 0, 1 \qquad l \in H$$

The first constraint is simply an overall material balance for the primary transfer network. The second set of constraints stems from Eq. 9b; they are used to identify the pinch location (by examining the solution to see which constraint is active) in the primary transfer network. The third and fourth constraints are concerned with the regeneration network and are analogous to the first and second ones. The fifth (sixth) set of constraints represent the bounds on the flow rates of the lean streams (regenerating agents). The seventh set of constraints provides the feasibility region (imposed by thermodynamics) for the composition of each regenerable lean stream as described by Eqs. 24–27. These constraints are used to reduce the size of the search space. The rest of the constraints are equivalent to Eqs. 12–15 and 18–21. Their purpose is to identify the values of the binary integer variables.

The above formulation is a mixed-integer nonlinear program (MINLP) whose structure suggests that it be solved using the generalized Benders decomposition method (Geoffrion, 1972), as demonstrated in the Appendix. The application of this method to the above problem provides the attractive property of guaranteed global solutions for both the subproblem and the master problem.

Now that we have addressed our first design target, we proceed to the second: the problem of minimizing the number of exchangers.

Network Synthesis

The solution of the foregoing minimum utility cost problem provides us with the flow rates of all the lean streams and regenerating agents, the supply and target compositions of all the regenerable lean streams, and the pinch locations in each of the two networks. With this information at hand, one can synthesize each network separately. The first step in synthesizing the primary transfer MEN is to construct its composition internal diagram (CID) as described in the Problem Characteristics section. The highest composition intervals will be denoted by $k = 1$ and the lowest by $k = n_{int}$. As previously mentioned, when n_p pinch points exist the synthesis problem can be decomposed into $n_p + 1$ subnetworks, where each two consecutive subnetworks are separated by a pinch. The subnetworks will be denoted by SN_m, $m=1,2...,n_p + 1$. It is therefore useful to define the following subsets:

$$R_m = \{i | i \in R, \text{stream } i \text{ exists in } SN_m\} \quad (28)$$

$$S_m = \{j | j \in S, \text{stream } j \text{ exists in } SN_m\} \quad (29)$$

$$R_{m,k} = \{i | i \in R_m, \text{stream } i \text{ exists in interval } \bar{k} \leq k; \bar{k}, k \in SN_m\} \quad (30)$$

$$S_{m,k} = \{j | j \in S_m, \text{stream } i \text{ exists in interval } k \in SN_m\} \quad (31)$$

Within any subnetwork, the freedom of stream matching is not prejudiced by any thermodynamic constraints. Since the mass exchanged between any two streams is bounded by the smaller of the two loads, the upper bound on the exchangeable mass between streams i and j in SN_m is given by

$$U_{i,j,m} = \min\left\{\sum_{k \in SN_m} W^R_{i,k}, \quad \sum_{k \in SN_m} W^S_{j,k}\right\} \quad (32)$$

Now, we define the binary variable $E_{i,j,m}$, which takes the value of 0 when there is no match between streams i and j in SN_m, and takes the value of 1 when a match exists between streams i and j (and hence an exchanger) in SN_m. Based on Eq. 32, one can write

$$\sum_{k \in SN_m} W_{i,j,k} - U_{i,j,m} E_{i,j,m} \leq 0$$
$$i \in R_m, j \in S_m, m = 1, 2, \ldots, n_p + 1 \quad (33)$$

where $W_{i,j,k}$ denotes the mass exchanged between the ith rich stream and the jth lean stream in the kth interval.

The following mathematical program is motivated by the analogous heat exchange network transshipment model proposed by Papoulias and Grossmann (1983). In the following program, we regard the rich streams as sources, the composition intervals as the intermediate nodes, and the lean streams as destinations. Therefore, the mixed-integer linear programming (MILP) transshipment formulation for minimizing the number of mass-exchanger units is given by

$$\min E = \sum_{m=1}^{n_p+1} \sum_{i \in R_m} \sum_{j \in S_m} E_{i,j,m} \quad \text{(P2)}$$

subject to

$$\delta_{i,k} - \delta_{i,k-1} + \sum_{j \in S_{m,k}} W_{i,j,k} = G_i(y_k - y_{k+1})$$
$$i \in R_{m,k}, k \in SN_m, m = 1, 2, \ldots, n_p + 1$$

$$\sum_{i \in R_{m,k}} W_{i,j,k} = L_j(x_{j,k} - x_{j,k+1})$$
$$j \in S_{m,k}, k \in SN_m, m = 1, 2, \ldots, n_p + 1$$

$$\sum_{k \in SN_m} W_{i,j,k} - U_{i,j,m} E_{i,j,m} \leq 0$$
$$i \in R_m, j \in S_m, m = 1, 2, \ldots, n_p + 1$$

$$\delta_{i,k} \geq 0 \qquad i \in R_{m,k}, k \in SN_m, m = 1, 2, \ldots, n_p + 1$$

$$W_{i,j,k} \geq 0 \qquad i \in R_{m,k}, j \in S_{m,k}, k \in SN_m, m = 1, 2, \ldots, n_p + 1$$

$$E_{i,j,m} = 0, 1 \qquad i \in R_m, j \in S_m, m = 1, 2, \ldots, n_p + 1$$

The above program is a MILP that is solved using the computer code LINDO (Schrage, 1984). The solution of program P2 provides information on the set of stream matches that must take place, the composition intervals over which mass is exchanged, and the amount of mass that must be exchanged in each match. Furthermore, it informs the designer whether or not stream splitting is required, and the composition intervals over which a stream ought to be split. It is interesting to note that the solution of program P2 may not be unique. However, one is able to generate all the solutions by adding integer-cut constraints that exclude previously obtained solutions from further consideration. For example, any previous solution can be eliminated by requiring that the sum of $E_{i,j,m}$ that were nonzero in that solution be less than the minimum number of exchangers. The selection of the final network from all the generated alternatives can be based upon the total network cost, operability, controllability, and so on.

The MILP transshipment formulation, P2, can also be used to minimize the number of mass exchangers in the regeneration network. This is done by constructing the CID for the regeneration network and letting the regenerable lean streams and the regenerating agents play the roles of the rich streams and the lean streams, respectively, in P2. After all, the regeneration network is another MEN.

As previously mentioned, by solving P2 one can determine the set of stream pairings as well as the exchanged load and location of each match. This information provides a complete description of the network structure. Having identified the configuration of the network with all the matches, one can design each mass-exchanger unit based upon the standard mass-transfer design procedures, or by employing commercially available process simulators that perform the suboptimization of each separation unit.

It is worth pointing out that in the foregoing programs P1 and P2 the values of the minimum allowable composition differences ought to be known prior to solving these programs. In general, the problem of minimizing the total annualized cost of the primary transfer and regeneration MENs can be addressed by a two-level optimization approach. In the lower level, programs P1 and P2 are solved for fixed values of the minimum allowable composition differences. In the upper level, a nonsmooth optimization problem is solved with the objective of identifying the optimal vector of minimum allowable composition differences that minimizes the total annualized cost of both MENs. A detailed description of this procedure is presented in a relevant research work (El-Halwagi and Manousiouthakis, 1990).

In the following example problem, we illustrate the usefulness of programs P1 and P2 in synthesizing the primary transfer and regeneration MENs. The problem formulation and data are basically adopted from the following references: Neufeld (1984), Berkowitz (1979), Lanouette (1977), Lewis and Martin (1967).

Example: Removal/Recovery of Phenols from the Waste Streams of a Coal Conversion Plant

The primary objective of a synthetic fuels plant is simply to convert a solid energy resource, coal, into more readily usable energy forms such as gaseous or liquid fuels. Coal conversion systems may be classified into two subsystems, coal gasification and coal liquefaction. Coal gasification yields a wide variety of useful products, such as medium-Btu gas (MBG), which is produced by gasifying coal with oxygen and steam, and low-Btu gas (LBG), which results from gasifying coal with air and steam. Coal liquefaction is based upon the hydrogenation of coal at high temperature and pressure to yield offgases, liquid fuels, and solid residues.

Coal conversion plants produce several aqueous waste streams that, if disposed of or recycled to the process without proper treatment, would cause serious health, environmental, and technical problems. The principal organic hazardous species in these liquid effluents is phenols. Indeed, the aqueous waste streams of coal conversion plants are the major contributors to the phenolic contamination of water supplies. The main environmental impact of discharging phenols into natural water resources is their detrimental effect to aquatic lives due to toxicity, oxygen depletion, and turbidity. Furthermore, if present in drinking water supplies, phenols (even at extremely low concentrations; parts per billion) impart unpleasant taste and odor to potable water. Finally, aside from its positive environmental impact, the removal/recovery of phenol from wastewater may be an economically attractive proposition, since phenol is a valuable chemical feedstock.

Figure 3 depicts a simplified flowsheet of a coal conversion plant. This plant comprises a gasification and a liquefaction unit. Coal is fed into the top of the gasifier, where it is contacted countercurrently with an oxygen–steam mixture. The offgas leaving the gasifier is quenched in a spray washer with recycled

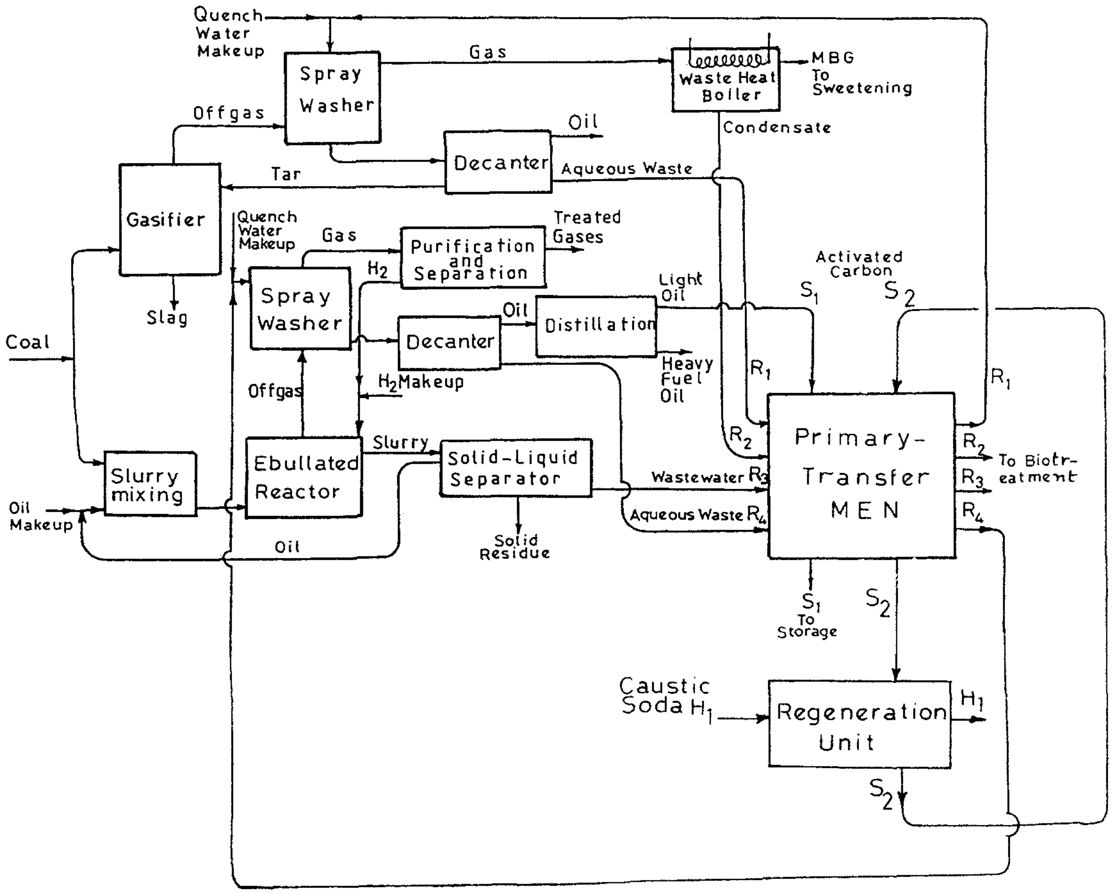

Figure 3. Simplified flowsheet for a coal conversion plant.

treated wastewater. The liquid effluent is passed to an oil–water–tar separator, from which the wastewater stream, R_1, is continuously withdrawn. The offgas is further cooled when passed through a waste heat boiler (WHB) that recovers latent heat from the gas by condensing the vapor on the boiler surfaces. The phenolic-based condensate, R_2, leaving the WHB contains, beside phenolics, dissolved organic and inorganic species, ammonia, and acid gases. The high phenol content of this condensate suggests that phenol ought to be recovered from this stream as a salable byproduct. Next, the offgas is sent to a scrubber where it is sweetened and purified.

The first step in the coal liquefaction unit is to mix and preheat the pulverized coal with oil. The slurry as well as compressed hydrogen is fed to the bottom of an ebullated-bed catalytic reactor, Table 1. The slurry stream leaving the reactor is dispatched to a solid–liquid separator where it is separated into three phases: oil, which in turn is recycled back to the slurry-preparation vessel; aqueous waste stream R_3, which ought to be dephenolized; and a solid residue. The gaseous stream leaving the top of the reactor is first quenched in a spray washer and then sent to a purification and separation unit where the hydrocarbon gas is separated from hydrogen, which is recycled to the reactor. The aqueous stream leaving the spray washer is decanted to separate a wastewater stream, R_4, from an oil stream. The oil stream is fractionated to produce heavy fuel oil as a bottom product and light distillate oil as a top product. This light oil consists mainly of a benzene–toluene–xylene (BTX) mixture and can be used as a solvent for the extraction of phenols (process MSA, S_1). Besides the purification of the waste streams, the transfer of phenols to the light oil is a beneficiary process for the oil stream itself. Phenols tend to act as oxidation inhibitors and serve to improve color stability and reduce sediment formation during the storage of light distillate oil.

One way of treating the liquid waste streams is through mass-exchange operations, which may be followed by biological treatment. Although phenols are inherently biodegradable, direct biotreatment of raw coal conversion wastewaters is not possible. The existence of phenols at high concentrations and their interaction with other substances dissolved in the aqueous wastes may cause ultimate failure of the biological treatment unit. Therefore, substantial removal of phenols from the waste streams ought to be achieved prior to any biotreatment.

After leaving the primary transfer MEN, the spent activated carbon ought to be regenerated so that it may be recycled back to the MEN. This is achieved by contacting it with caustic soda, which strips the adsorbed phenol by solvating it and then reacting with it to form sodium phenolate (a salable chemical). The rate of reaction is mass-transfer controlled, and therefore the contactor may be designed as a solvent extraction column.

The design task is to synthesize cost-effective primary transfer and regeneration MENs that can remove/recover phenols from the rich streams R_1, R_2, R_3, and R_4 and regenerate S_2. Available for service as lean streams are light distillate oil, S_1, and activated carbon, S_2. Also, available for service is caustic soda, H_1, for the regeneration of the spent adsorbent S_2 leaving the primary transfer MEN.

Within the range of compositions involved, the following equilibrium relations can be used for phenol in S_1 and S_2, respectively:

$$y = 0.71x_1 + 0.001$$

$$y = 0.13x_2 + 0.001$$

On the other hand, the equilibrium relation for phenol in H_1 is given by

$$x = 1.38z_1$$

A single value of 0.0001 for the minimum allowable composition differences for all the pairs of streams will be used. The unit costs associated with each MSA or regenerating agent are 0.01 \$/kg of S_1, 0.07 \$/kg of S_2, and 0.015 \$/kg of H_1.

Solving P1 and P2, one obtains the minimum-utility MEN for this example, Figure 4. Each exchanger is represented by two circles connecting the matched pair of streams. Mass-exchange loads (kg/s) are noted beneath each exchanger and compositions (wt. %) are placed above the arrows representing the streams. The overall network features four extractors, one adsorption column, and one regenerator (desorption column). The optimal flow rates of S_1, S_2, and H_2 are 9.6000, 0.2215, and 0.3260 kg/s, respectively. The optimal supply and target compositions of S_2 are 0.014 and 0.75 wt. %, respectively.

Conclusions

We have addressed the problem of simultaneously synthesizing primary transfer and regeneration MENs. The problem was dealt with in two stages. In the first stage a mixed-integer nonlinear program was formulated with the objective of minimizing the cost of the lean streams and the regenerating agents while insuring thermodynamic feasibility of mass exchange. The solution was carried out by means of the generalized Benders decomposition method to provide the optimal flow rates of all the lean streams and the regenerating agents as well as the pinch locations. This target is achieved ahead of design and without any prior commitment to the network structure. Next, a mixed-integer linear program was formulated and solved to generate both the primary-transfer and the regeneration MENs that feature the smallest number of mass-exchanger units satisfying the minimum operating cost. An example problem on

Table 1. Stream Data for Phenol Recovery/Removal Example

Rich Streams				Lean Streams				Regenerating Agents			
Stream	G_i kg/s	y_i^s	y_i^t	Stream	L_j^c kg/s	x_j^s	x_j^t	Stream	M_l^c	z_l^s	z_l^t
R_1	3.3	0.05	0.0015	S_1	10.0	0.0013	0.0250	H_1	10.0	0.000	0.005
R_2	0.6	0.07	0.0030	S_2	10.0	—	—	—	—	—	—
R_3	1.4	0.02	0.0030	—	—	—	—	—	—	—	—
R_4	0.2	0.03	0.0020	—	—	—	—	—	—	—	—

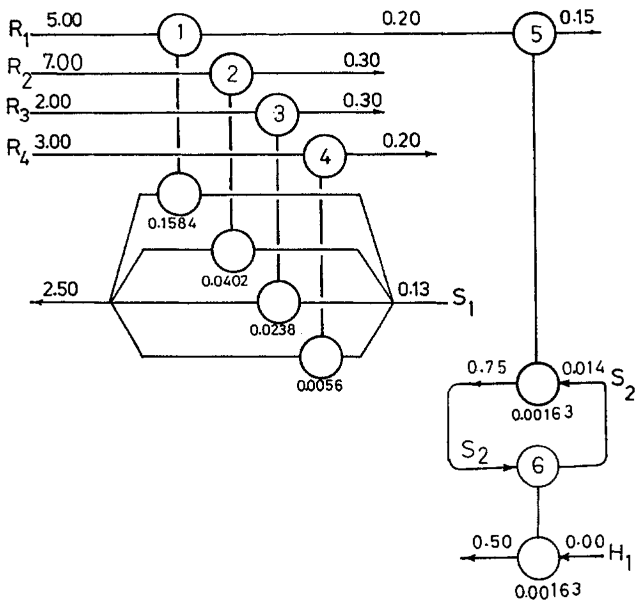

Figure 4. Simultaneously synthesized primary transfer and regeneration mass-exchange networks.

the removal of phenols from the wastes of a coal conversion plant was solved to elucidate the merits offered by the proposed synthesis approach.

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Notation

b_j = intercept of equilibrium line for lean stream j
b_l = intercept of equilibrium line for regenerating agent l
c_j = unit cost of lean stream j, \$/kg
c'_l = unit cost of regenerating stream l, \$/kg
$E_{i,j,m}$ = a mass exchanger for streams i and j in subnetwork m
G_i = mass flowrate of rich process stream i, kg/s
H = set of regenerating agents
i = index for rich streams
j = index for lean streams
k = index for composition intervals
l = index for regenerating agents
L_j = mass flow rate of lean stream j, kg/s
L_j^c = upper bound on mass flow rate of lean stream j, kg/s
m = index for subnetworks
m_j = slope of equilibrium line for lean stream j
m'_l = slope of equilibrium line for regenerating agent l
M_l = flow rate of regenerating agent l, kg/s
M_l^c = upper bound on flow rate of regenerating agent l, kg/s
n_i = number of independent problems in the network
n_{int} = number of composite intervals in the CID
n_p = number of mass-exchange pinch points in the problem
N_H = number of regenerating agents
N_i = number of independent subproblems for primary transfer MEN
N'_i = number of independent subproblems for regeneration MEN
N_R = number of rich streams
N_S = number of lean streams
N_{SO} = number of once-through lean streams
N_{SR} = number of regenerable lean streams
p = index for pinch-point candidates in primary transfer MEN
P = set of pinch-point candidates in primary transfer MEN
q = index for pinch-point candidates in regeneration MEN
Q = set of pinch-point candidates in regeneration MEN
R = set of rich streams
S_m = set of lean streams existing in subnetwork m, Eq. 29
$S_{m,k}$ = defined by Eq. 31
S_m = subnetwork m
$U_{i,j,m}$ = upper bound on mass that can be exchanged between streams i and j in subnetwork m, Eq. 32
$W_{i,j,k}$ = mass exchanged between streams i and j in interval k, kg/s
$W^R_{i,k}$ = mass-exchange load of rich stream i in interval k, kg/s
$S^S_{j,k}$ = mass-exchange load of lean stream j in interval k, kg/s
x_j = mass fraction of the key component in lean stream j
x_j^c = upper bound on mass fraction of key component in lean stream j
x_j^l = lower bound on mass fraction of key component in lean stream j
x_j^{max} = maximum practically feasible outlet mass fraction
x_j^s = supply mass fraction of key component in lean stream j
x_j^t = target mass fraction of key component in lean stream j
x_j^* = equilibrium outlet mass fraction of key component in lean stream j
y = mass fraction of key component in any rich stream
y_i^s = supply mass fraction of key component in rich stream i
y_i^t = target mass fraction of key component in rich stream i
z_l = mass fraction of key component in regenerating agent l
z_l^c = upper bound on mass fraction of key component in regenerating agent l
z_l^s = supply mass fraction of key component in regenerating agent l
z_l^t = target mass fraction of key component in regenerating agent l

Subscripts

i = rich stream i
j = lean stream j
k = kth composition interval
m = mth subnetwork

Superscripts

p = pinch point candidate in primary transfer MEN
q = pinch point candidate in regeneration MEN
s = supply
t = target

Greek letters

$\delta_{i,k}$ = residual mass exchange load leaving interval k for rich stream i, kg/s
$\epsilon_{i,j}$ = minimum allowable composition difference for the pair of streams i and j
$\lambda^s_{i,p}$ = binary integer variable, Eq. 13
$\lambda^t_{i,p}$ = binary integer variable, Eq. 12
$\eta^s_{i,p}$ = binary integer variable, Eq. 15
$\eta^t_{i,p}$ = binary integer variable, Eq. 14
$\psi^s_{j,q}$ = binary integer variable, Eq. 18
$\psi^t_{j,q}$ = binary integer variable, Eq. 19
$\phi^s_{l,q}$ = binary integer variable, Eq. 20
$\phi^t_{l,q}$ = binary integer variable, Eq. 21

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Appendix: Solution of the Minimum Utility Cost Problem (P1) via Generalized Benders Decomposition

The minimum utility cost problem, P1, is a MINLP whose solution can be effectively carried out through a special decomposition algorithm. Here we briefly present how the generalized Benders decomposition (GBD) method may be employed to solve P1. Geoffrion (1972) devised a projection approach that decomposes the original optimization problem into two subproblems by employing the concept of partitioning and the theory of nonlinear duality. The GBD is concerned with problems of the form

$$\min_{u,v} f(u, v) \qquad \text{(P3)}$$

subject to

$$g(u, v) \leq 0$$

where v is a vector of complicating variables in the sense that P3 is a much easier optimization problem in u when v is temporarily held fixed. The GBD technique decomposes problem P3 into a subproblem and a master problem. The subproblem is the original problem, P3, solved for some fixed value of v denoted by v^n:

$$\min_{u} f(u, v^n) \qquad \text{(P4)}$$

subject to

$$g(u, v^n) \leq 0$$

The solution of this problem provides an upper bound on the solution of the original problem, P3. In turn, the master problem is obtained by projecting P3 onto v and by invoking nonlinear duality and constraint relaxation concepts. The relaxed master problem progressively incorporates constraints at each iteration in such a way that the feasibility region is continuously shrunk until an optimal solution (or no feasible solution) is found. The master problem is given by:

$$\min_{v,Q} Q \qquad \text{(P5)}$$

subject to

$$Q \geq \min_{u} \{f(u, v) + (\alpha^t g(u, v)\} \qquad \forall\, \alpha \geq 0$$

$$\min_{u} \{(\beta^t g(u, v)\} \leq 0 \qquad \forall\, \beta \geq 0, \quad \|\beta\|_1 = 1$$

The solution of P5 presents a lower bound on the solution of the original problem, where α is the optimal (near-optimal) multiplier vector associated with the solution of the subproblem, and β^n is the vector of dual prices for the nth infeasible subproblem. Every time the solution of the subproblem is feasible, one additional constraint of the foregoing first set of constraints is added to the master problem. On the other hand, whenever the solution of the subproblem is infeasible, an extra constraint of the second set of constraints is included in the master problem.

In order to apply GBD to the solution of P1, we first select the vector of supply and target compositions of the regenerable lean streams to be our complicating vector, that is,

$$v^t = [x^s_{SO+1}\ x^s_{SO+2} \ldots x^s_{SO+SR}\ x^t_{SO+1}\ x^t_{SO+2} \ldots x^t_{SO+SR}] \qquad \text{A1}$$

By solving the master problem, one obtains an updated value of v^n that is passed on to the subproblem and the previous procedure is repeated. Hence, the above procedure is continued until the values of the subproblem and the master problem do not change any further. It is interesting to note that each of the subproblems and the master problem can be solved globally for their respective optima. Hence, depending upon the implementation of the procedure, it is likely to obtain the global optimum of the original problem (Floudas et al., 1989) or to identify global bounds on the solution.

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