Variable Target Mass-Exchange Network Synthesis through Linear Programming

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A mass-exchange network (MEN) synthesis problem is considered with streams whose target compositions are allowed to vary between upper and lower bounds. The design task is to determine the minimum mass separating agent (utility) cost needed for the transfer of a single component from the rich to the lean streams. The mathematical formulation of this synthesis problem leads to a mixed integer nonlinear program. In this work, we propose a novel formulation of the problem that leads to a linear program. Stream decomposition is employed in attaining this novel linear programming formulation and rigorous proofs are presented which establish that the two formulations have the same solution. The linear programming formulation reduces the complexity of the considered MEN synthesis problem, thus making feasible its solution even for large-scale problems. Two examples, illustrating the procedure, are presented. Both demonstrate that significant utility cost savings can be achieved over the fixed composition MEN synthesis problem.

Introduction

Mass exchange includes the unit operations of absorption, adsorption, liquid-liquid extraction, desorption, and stripping. The operating utilities for these operations are mass separating agents (MSA) such as adsorbents, ion-exchange resins, or solvents, just as steam and cooling water are some of the operating utilities for heat exchange. The design of these separation systems involves choosing the appropriate MSAs and determining their optimal flow rates to achieve the specified recovery of the key component.

Separation system synthesis has been pursued through a variety of approaches, some of which include those of Rudd et al. (1973), Lu and Motard (1985), and Lo et al. (1983). More recently, the area of mass-exchange network (MEN) synthesis has been a hot bed of research activity in separation synthesis. MEN synthesis was introduced (El-Halwagi and Manousiouthakis, 1989) in analogy to heat-exchange network synthesis to provide a rigorous tool for the synthesis and evaluation of mass-exchanger based separation networks that can achieve specified targets at minimum cost. Isothermal MEN synthesis problems involving a single transferable component (El-Halwagi and Manousiouthakis, 1989) simultaneous synthesis of an MEN and its regeneration network (El-Halwagi and Manousiouthakis, 1990b), stream-dependent multiple equilibria (El-Halwagi and Manousiouthakis, 1990a), variable targets (Gupta and Manousiouthakis, 1993), chemical absorption (El-Halwagi and Srinivas, 1992), nonlinear equilibria (Gupta and Manousiouthakis, 1993; Srinivas and El-Halwagi, 1994), and multiple component targets (Gupta and Manousiouthakis, 1994) have now been solved. Distillation has also been shown to be representable as an interactive HEN/MEN network through the novel "state-space" approach to process synthesis (Bagajewicz and Manousiouthakis, 1992).

With MEN synthesis, a systematic tool has been made available to evaluate separation technologies and design recycling networks for hazardous waste minimization. Waste minimization involves the removal and reuse of waste components from chemical plant effluents prior to their disposal. In-plant reuse of toxic substances reduces the total harmful effluents of a plant and generates recyclable streams, thereby reducing the operating cost of process plants (Hunt and Schecter, 1989). MEN synthesis applications to waste minimization have been investigated for waste streams with multicomponent targets (Gupta and Manousiouthakis, 1994), for solvent recovery networks employing the state-space ap-

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proach (Bagajewicz and Manousiouthakis, 1992), and for dephenolization in a petroleum refinery (El-Halwagi et al., 1992). Wang and Smith (1994) proposed the solution of an MEN-like synthesis problem for wastewater minimization where the only lean utility is water. Their problem formulation avoids the explicit use of the "rich composite curve" by employing the notion of "a limiting water profile" that accounts for both rich stream and driving force information.

The classical MEN synthesis minimum utility cost problem is as follows:

"Given a set of rich streams, $R \triangleq \{R_i | i = 1, \ldots, N_R\}$, with known flow rates, inlet and outlet compositions for a single component and a set of lean streams and utilities, $S \triangleq \{S_j | j = 1, \ldots, N_S\}$, with known costs, inlet and target compositions for the same component; determine the minimum utility cost for the separation."

Implicit in the above problem statement is the assumption that there are no temperature changes within the MEN. Finding the minimum utility consumption for this fixed target MEN synthesis task is formulated as a linear program (LP) (El-Halwagi and Manousiouthakis, 1990a) in a manner similar to the LP minimum utility cost formulation for fixed target HEN synthesis (Papoulias and Grossmann, 1983). The minimum utility cost problem becomes a mixed integer nonlinear program (MINLP) for mass-exchange networks that include regeneration (El-Halwagi and Manousiouthakis, 1990b). The MEN framework rigorously incorporates thermodynamic constraints and can be used for the selection of the mass separation utilities and the calculation of their minimum cost. Once the minimum utility cost is determined, without any prior commitment to the network structure, a network realizing this operating cost is synthesized.

In an earlier article (Gupta and Manousiouthakis, 1993), we generalized the separation task to tackle real situations where supply and target compositions of the rich and lean streams are allowed to vary within upper and lower bounds. In that work, the advantages of having variable stream compositions at the design stage were demonstrated. The mathematical formulation of this MEN synthesis problem led to a mixed integer nonlinear program (MINLP). This program was shown to possess certain properties which, in turn, were employed to develop a solution procedure. This procedure was guaranteed to converge to the *global* optimum.

In the next section, we outline the conceptual variable target MEN synthesis problem, and briefly summarize the assumptions and thermodynamic background required for the problem formulation. In the following section, two mathematical representations for this problem are presented, one that is an MINLP, and the other that is an LP. These two problems are shown to be equivalent through a theorem in the next section. Finally, two waste minimization case studies are solved to illustrate the savings obtainable through variable target MEN synthesis, and to demonstrate the use of the LP formulation for obtaining this solution.

Preliminaries

In many MEN synthesis case studies, such as those in waste minimization, the inlet and outlet compositions of the lean or rich streams are specified only in terms of a maximum or minimum allowable composition. For instance, if the lean streams are process streams, then downstream process requirements may impose upper and lower bounds on the outlet compositions of these lean streams. Then, the problem specification is that the exit (inlet) composition of a lean stream should lie within a given range of compositions. Similarly, upstream processes in the chemical plant may lead to streams whose supply compositions may also lie within a range of compositions. For these practical situations, the problem formulation should incorporate the bounds on the stream compositions as constraints, letting the actual inlet or outlet composition be *variable*. Examples include phenol recovery from lube oil refinery wastewaters in Lewis and Martin (1967), or acrolein reduction in the effluents of a petrochemical plant.

Considering variable targets on stream outlet compositions is not only more realistic, but can also lead to savings in the utility cost. For example, if there are multiple lean streams in the MEN, each with a different cost, and a cheap lean stream has a fixed target composition that renders it infeasible, then the obtained network may not have the minimum possible cost since this stream was not used. By allowing the outlet composition of this cheap lean stream to vary, one may make it feasible, thus decreasing the duty on the more expensive lean stream(s). This will lower their flow rate, and a lower total utility cost will be achieved.

Another advantage of variable targeting is that in some instances, the rich streams can be cleaned more than a fixed target specification at no additional cost. Consider a rich stream with a fixed exit composition above the actual exit composition of a lean stream (on a CID-scale). If the target composition of the lean stream is below its upper bound, the rich stream target composition can be lowered. As a result, the rich load in the upper intervals of the lean stream increases, which can be balanced by raising the outlet composition of the lean stream, *without* increasing its flow rate. In effect, key component recovery is enhanced without any change in the utility cost of the network. This may lead to savings in the downstream processing costs of the rich stream.

This so-called variable target mass-exchange synthesis problem, shown in Figure 1, can be stated as:

"Given a set of rich streams, $R \triangleq \{R_i | i = 1, \ldots, N_R\}$, with known flow rates, inlet compositions and upper and lower bounds on target compositions for a single component, and a set of lean streams and utilities, $S \triangleq \{S_j | j = 1, \ldots, N_S\}$, with their known costs, inlet compositions and upper and lower bounds on target compositions for the same component; determine the minimum utility cost for the separation."

For each element of the set R or S the inlet composition, and upper and lower bounds on the outlet composition are known. For elements of the set R, the flow rates are known, while for elements of the set S, only upper bounds on the flow rates may be imposed.

In this work, only this so-called variable target problem is considered. Indeed, when supply compositions are also allowed to vary, Gupta and Manousiouthakis (1993) have proved the following property:

Property 1. When the inlet compositions of the rich and lean streams are allowed to vary between upper and lower bounds, the minimum utility cost solution of the variable supply and target problem will always feature all the variable supply compositions at their lower bounds.

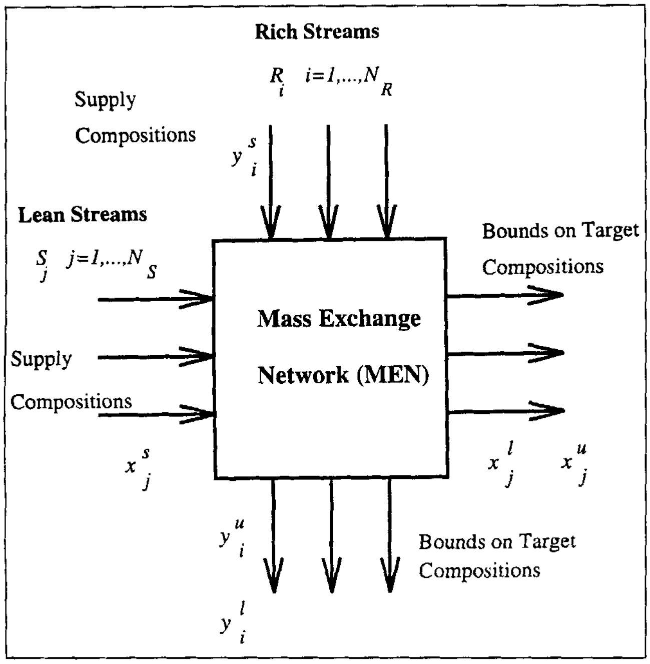

Figure 1. Variable target MEN synthesis problem.

This property implies that the minimum utility (MSA) cost problem with variable supply and target compositions is equivalent to a problem with only variable target compositions and all the stream supply compositions are fixed at their lower bounds.

Besides the specifications of the rich and lean streams themselves, thermodynamic relations that govern the mass transfer between these streams are also required for the synthesis of an MEN. Any mass-transfer operation is considered to be feasible if it satisfies the law of conservation of mass and the second law of thermodynamics. The law of conservation of mass states that the mass gained by the lean streams must equal the mass lost by the rich streams. This law should hold for both the total mass and the mass of every species in the streams. This law, in analogy with the first law of thermodynamics (the law of conservation of energy), will be referred to as the first law hereafter.

The second law of thermodynamics (Reid, 1960, p. 20) states that:

"There exists an intensive property, T, (which is always positive) and an additive-extensive property, S, such that $dQ = TdS$ for reversible processes, and $dQ < TdS$ for irreversible processes."

Here, T is the process temperature, S is the entropy, and Q is the heat input to the system. Consider now a closed system consisting of two phases, denoted as α and β, in thermal equilibrium at temperature T. Let a small molar amount of species i, dn_i, spontaneously transfer from α to β. For this system, the change in internal energy, U, due to the transfer of i is given by (Reid, 1960, p. 149)

$$dU = TdS + dW - (\mu_i^\alpha - \mu_i^\beta)dn_i$$
$$\Rightarrow (\mu_i^\alpha - \mu_i^\beta)dn_i = TdS - (dU - dW) = TdS - dQ, \quad (1)$$

where W is the work output from the system, μ_i^α is the chemical potential (also known as the partial molar Gibbs free energy) of species i in phase α, and μ_i^β is similarly the chemical potential of species i in phase β. The aforementioned second law of thermodynamics then implies that the right-hand side of Eq. 1 is nonnegative. Therefore, mass transfer of i from α to β can occur if μ_i^α is greater than or equal to μ_i^β. Mathematically: $\mu_i^\alpha \geq \mu_i^\beta$. Thus the difference between the chemical potential of the two phases, μ_i^α and μ_i^β can be considered as the driving force for mass transfer.

The chemical potential μ_i^α (or μ_i^β) depends in general on the temperature, pressure, and composition of all species in the phase α (or β). However, under certain circumstances, this dependence can be simplified to the point that μ_i^α (or μ_i^β) depends only on the composition of species i in phase α (or β), y_i (or x_i). Then, the mathematical condition for mass transfer can be stated as $\mu_i^\alpha(y_i) \geq \mu_i^\beta(x_i)$. Mathematical manipulations can then transform this condition to the form $y_i \geq f(x_i)$ or equivalently $f^{-1}(y_i) \geq x_i$, if $f(\bullet)$ is a monotonic function. Let us now illustrate this transformation for two ideal phases that are at the same temperature T and pressure P, and in contact with each other.

Let α be an ideal gas at pressure P, where the partial pressure of species i is $p_i = y_i P = n_i/n$ (Smith and Van Ness, 1987, p. 300). Also, the entropy of the gas can be calculated from the relation $dS_i^\alpha = -Rd\ln P$ (Smith and Van Ness, 1987, p. 171). Substituting in the Gibbs energy relation $G^\alpha = H^\alpha - TS^\alpha$, and employing the Gibbs theorem (Smith and Van Ness, 1987, p. 300), yields the following expression for μ_i^α (Smith and Van Ness, 1987, p. 302)

$$\mu_i^\alpha = G_i^\alpha + RT \ln y_i, \quad (2)$$

where T is the temperature of the gas.

Now, let β be an ideal liquid solution. Then, the solution properties are: $V^\beta = \Sigma x_i V_i$, where V is the solution volume and x_i is the mole fraction of species i; $S^\beta = \Sigma x_i S_i - R\Sigma x_i \ln x_i$; and $G^\beta = H^\beta - TS^\beta$. Thus, μ_i^β is shown to be (Smith and Van Ness, 1987, p. 302)

$$\mu_i^\beta = G_i^\beta + RT \ln x_i, \quad (3)$$

Mass transfer from the rich phase α to the lean phase β requires that the second law of thermodynamics be satisfied

$$\mu_i^\alpha \geq \mu_i^\beta.$$

Substituting Eqs. 2 and 3, we obtain

$$G_i^\alpha + RT \ln y_i \geq G_i^\beta + RT \ln x_i,$$
$$\Rightarrow G_i^\alpha - G_i^\beta \geq RT \ln \frac{x_i}{y_i},$$

Since $dG_i^\beta = V_i^\beta dP$, and G_i^β is assumed independent of P, the lefthand side of the above relation is $RT \ln (P/P_i^{\text{sat}})$, where, the P_i^{sat} is the saturation pressure of species i (Smith and Van Ness, 1987, p. 304). Then, the above relation can be stated as

$$RT \ln \frac{P}{P_i^{\text{sat}}} \geq RT \ln \frac{x_i}{y_i}, \qquad \Rightarrow x_i \leq \frac{P}{P_i^{\text{sat}}} y_i \;\hat{=}\; K_i^{-1} y_i, \quad (4)$$

which is of the form $x_i \leq f^{-1}(y_i)$.

The aforementioned thermodynamic feasibility condition for the transfer of component i, hereafter referred to as the second law of thermodynamics, can be represented on a composition interval diagram (CID) by establishing an equivalence between the rich and lean composition scales through the equilibrium relation. Then, second law feasibility simply states that a rich stream with composition y can transfer mass to any lean stream with composition $x \leq f^{-1}(y)$.

Let us now consider a countercurrent mass exchanger that transfers the key component from a rich stream, with supply composition y^s, outlet composition $y^t < y^s$ and flow rate G, to a lean stream, with supply composition x^s, outlet composition $x^t > x^s$ and flow rate L. Let also x and y represent the lean and rich key component compositions at an arbitrary cross-section of the exchanger. If the two streams have constant flow rates within the exchanger, then a mass balance yields

$$y = \frac{y^t - y^s}{x^s - x^t} x + \frac{y^s x^s - y^t x^t}{x^s - x^t} \quad (5)$$

$$\frac{L}{G} = \frac{y^t - y^s}{x^s - x^t} \quad (6)$$

Equation 5 represents the operating line, on a y-x diagram, which has a slope equal to the ratio of the lean to the rich flow rates, according to Eq. 6. This operating line should lie above the $y = f(x)$ equilibrium curve so that the second law requirement $y \geq f(x)$ is satisfied throughout the exchanger. If $f(x)$ is convex with respect to x, i.e., $\alpha f(x^s) + (1-\alpha) f(x^t) \geq f[\alpha x^s + (1-\alpha) x^t]$ for all $\alpha \in [0, 1]$, then the straight operating line remains above the equilibrium line if and only if $y^s \geq f(x^t)$ and $y^t \geq f(x^s)$, i.e., the end-point conditions of the exchanger satisfy thermodynamic feasibility.

The above discussion suggests the usefulness of a CID. In a CID, the supply compositions and the bounds on the target compositions of rich and lean streams (x^s, y^s and x^u, x^l, y^u, y^l) are employed to establish intervals in the diagram. Figure 2 shows such a diagram for one rich and one lean stream that together create three intervals numbered $k-1$, k, and $k+1$. Any rich stream with a supply composition y^s can be matched with a lean stream with a supply composition $x^s \leq f^{-1}(y^t)$ and a target composition $x^t \leq f^{-1}(y^s)$. Since x^s, x^t, y^s, and y^t are edges of the intervals, the second law thermodynamic requirement is automatically satisfied for the endpoint conditions of these streams, since the outlet compositions of both the rich and the lean stream are within the interval. Therefore, according to the above discussion if the equilibrium relation $f^{-1}(\bullet)$ is convex, the second law is satisfied throughout the match, and only first law requirements need be considered. An example of a convex equilibrium relation is the dilute solution Raoult's law (Eq. 4) like relation that is employed in the examples presented in this article

$$y = m_j(x + \epsilon_j) + b_j \quad \forall j = 1, \ldots, N_S \quad (7)$$

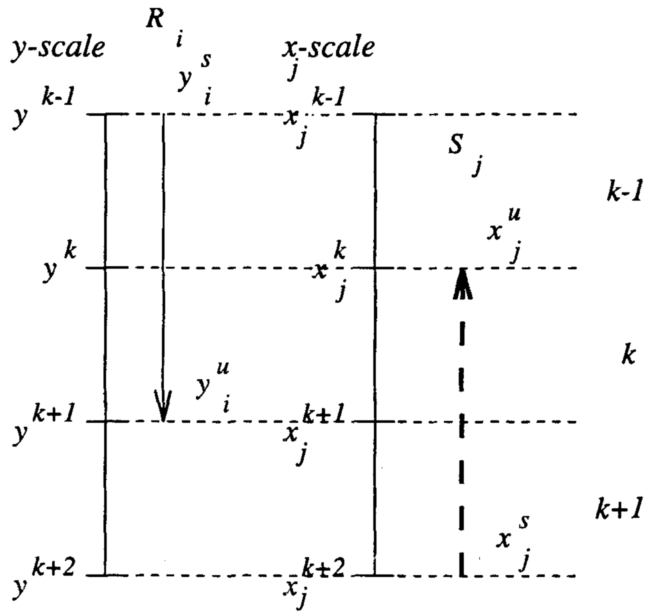

Figure 2. CID with one rich and one lean stream and the three intervals created due to inlet compositions, and the ranges on their outlet compositions.

$y_i^u = y_i^l$, and $x_j^s = x_j^l$.

where ϵ denotes the minimum allowable mass-transfer driving force in x composition units.

Note that sometimes the reverse notation is employed to describe the equilibrium relation, i.e., y denotes the key component composition in the lean phase that is in equilibrium (denoted as $y = f(x)$) with a key component composition x in the rich phase. In this case, a rich phase model load available at composition x can be transferred to any lean phase with composition $y \leq f(x)$. Then, to guarantee feasibility throughout the exchanger by ensuring feasibility only at the end points, this equilibrium relationship is required to be concave. Such notation is typically encountered in distillation, where the $y = f(x)$ equilibrium curve is given in terms of the most volatile component, thus, making the vapor phase lean with its composition indicated by y (Bagajewicz and Manousiouthakis, 1992). In this case, a typical concave equilibrium relation would be the binary vapor-liquid equilibrium with constant relative volatility α_j

$$y = \frac{\alpha_j x_j}{1 + (\alpha_j - 1) x_j}$$

Equilibrium relations that describe the transfer of the key component from the rich to the lean stream, and are nonconvex, can also be accommodated within this framework in a number of ways (Gupta and Manousiouthakis, 1993; Srinivas and El-Halwagi, 1994).

The variable target MEN synthesis problem also features a number of other well-known properties (Grimes, 1980; Cerda et al., 1983; El-Halwagi and Manousiouthakis, 1990b; Gupta and Manousiouthakis, 1993).

Property 2. At the minimum utility cost solution, there is no mass transferred across the pinch point, if one exists.

The pinch can occur only at the corner points (stream inlet and outlet compositions) in the common composition range of the composite curves. The following property determines which of all the corner points of the streams, can be pinch points:

Property 3. Only the inlets of the rich or lean streams in the common composition range of the y- and x-scales, are pinch point candidates.

Employing the above conceptual problem definition, thermodynamic information and the CID, and pinch properties, the mathematical problem formulation of the variable target MEN synthesis problem can be carried out, as shown next.

Mathematical Problem Formulation

MINLP formulation

An MINLP formulation of the variable target is developed in Gupta and Manousiouthakis (1993). That formulation quantifies the aggregate rich and lean loads below the pinch point candidates (stream inlet compositions) to determine the thermodynamic feasibility constraints for a given problem. The formulation proposed below alternatively quantifies the rich and lean loads within every interval of the CID to check for thermodynamic feasibility. The problem properties proven in Gupta and Manousiouthakis (1993) are valid for this MINLP formulation as well, and the same solution technique as before can also be employed. Nevertheless, this will not be necessary since the primary function of this proposed MINLP is to serve as a stepping stone to the LP based formulation of the variable target problem.

The employed symbol convention is as follows: for each element R_i of the set R we are given the flow rate G_i, the inlet concentration y_i^s and upper and lower bounds on the outlet composition y_i^u and y_i^l, respectively. Similarly, for S_j we are given its cost coefficient c_j, the inlet composition x_j^s, and the upper and lower bounds on the outlet composition x_j^u and x_j^l, respectively. The lean stream flows L_j and the actual lean and rich stream outlet compositions x_j^t and y_i^t, respectively, are to be determined.

Consider a simple CID as in Figure 2 with intervals corresponding to y_i^s, y_i^u, x_j^s, x_j^u, and x_j^l. The streams shown have $y_i^u = y_i^l$ and $x_j^s = x_j^l$, though in the general case this will not be true, and the CID may have two additional intervals. Let such a problem have a total of N_{int} intervals that are numbered from the top to the bottom of the CID.

The position of the ith rich streams with respect to the upper edge of the kth composition interval, y^k, is located through binary variables defined as

$$\lambda_{i,k}^t \triangleq \begin{cases} 1 \text{ if } y_i^t < y^k & i = 1,\ldots,N_R \\ 0 \text{ if } y_i^t \ge y^k & k = 1,\ldots,N_{\text{int}}+1, \end{cases}$$

$$\lambda_{i,k}^s \triangleq \begin{cases} 1 \text{ if } y_i^s < y^k & i = 1,\ldots,N_R \\ 0 \text{ if } y_i^s \ge y^k & k = 1,\ldots,N_{\text{int}}+1, \end{cases}$$

and the position of the jth lean stream relative to the upper edge of the kth composition interval, x_j^k, is located through analogous binary variables

$$\eta_{j,k}^t \triangleq \begin{cases} 1 \text{ if } x_j^t < x_j^k & j = 1,\ldots,N_S \\ 0 \text{ if } x_j^t \ge x_j^k & k = 1,\ldots,N_{\text{int}}+1, \end{cases}$$

$$\eta_{j,k}^s \triangleq \begin{cases} 1 \text{ if } x_j^s < x_j^k & j = 1,\ldots,N_S \\ 0 \text{ if } x_j^s \ge x_j^k & k = 1,\ldots,N_{\text{int}}+1, \end{cases}$$

Since the supply compositions y_i^s and x_j^s are known for every stream, the associated binaries $\lambda_{i,k}^s$ and $\eta_{j,k}^s$ are known. Furthermore, it also holds that $x_j^s \le x_j^t$ and $x_j^k \ge x_j^{k+1}$, hence, $\eta_{j,k}^s \ge \eta_{j,k}^t \ge \eta_{j,k+1}^t$. Similarly, $y_i^s \ge y_i^t$ and $y_i^k \ge y_i^{k+1}$, hence, $\lambda_{i,k}^t \ge \lambda_{i,k-1}^t \ge \lambda_{i,k}^s$.

The minimum utility cost problem formulation for MEN synthesis requires that a first law component balance around each interval be satisfied. The general expression for determining the load of any lean stream in the kth interval is

$$L_j\left[\eta_{j,k}^s\left(x_j^k - x_j^{k+1}\right) + \eta_{j,k}^t\left(x_j^t - x_j^k\right) - \eta_{j,k+1}^t\left(x_j^t - x_j^{k+1}\right)\right]. \tag{8}$$

Indeed, as illustrated in Figure 3, there are only seven possible positions of the supply and target compositions relative to the kth interval (since $\eta_{j,k}^s \ge \eta_{j,k}^t \ge \eta_{j,k+1}^t$). For each of these seven cases, it is established below that the above expression (Eq. 8) exactly quantifies the lean stream load in the kth interval:

(1) $\left(x_j^t < x_j^{k+1}\right) \Rightarrow \left(\eta_{j,k}^t = 1,\ \eta_{j,k+1}^t = 1,\ \eta_{j,k}^s = 1\right) \Rightarrow (8) = 0.$

(2) $\left(x_j^t = x_j^{k+1}\right) \Rightarrow \left(\eta_{j,k}^t = 1,\ \eta_{j,k+1}^t = 0,\ \eta_{j,k}^s = 1\right) \Rightarrow (8) = 0.$

(3) $\left(x_j^k > x_j^t > x_j^{k+1}\right) \Rightarrow \left(\eta_{j,k}^t = 1,\ \eta_{j,k+1}^t = 0,\ \eta_{j,k}^s = 1\right)$
$\Rightarrow (8) = L_j\left(x_j^t - x_j^{k+1}\right).$

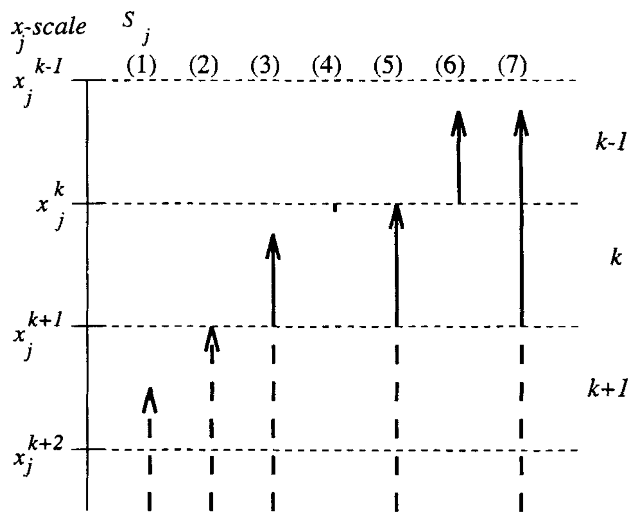

Figure 3. CID showing possible locations of the supply and target compositions of stream S_j, x_j^s and x_j^t, with respect to the top edge of the kth interval, x_j^k.

Solid line indicates the section of the stream that is definitely present; the dashed section may or may not be present.

The composition x_j^s is by definition of the CID the same as one of the x_j^m compositions, and hence, cannot be between x_j^k and x_j^{k+1}. If $x_j^s = x_j^k$, for any k, x_j^s is replaced by x_j^k.

$$(4)\ \left(x_j^t = x_j^k,\ x_j^s = x_j^t\right) \Rightarrow \left(\eta_{j,k}^t = 0,\ \eta_{j,k+1}^t = 0,\ \eta_{j,k}^s = 0\right) \Rightarrow (8) = 0.$$

$$(5)\ \left(x_j^t = x_j^k,\ x_j^s \neq x_j^t\right).$$

Since x_j^s is the same as one of the x_j^m compositions, $x_j^s \neq x_j^t \Rightarrow x_j^s \leq x_j^{k+1}$. Hence, $(x_j^t = x_j^k,\ x_j^s \neq x_j^t) \Rightarrow (\eta_{j,k}^t = 0,\ \eta_{j,k+1}^t = 0,\ \eta_{j,k}^s = 1) \Rightarrow (8) = L_j(x_j^k - x_j^{k+1})$.

$$(6)\ \left(x_j^t > x_j^k,\ x_j^s \geq x_j^k\right) \Rightarrow \left(\eta_{j,k}^t = 0,\ \eta_{j,k+1}^t = 0,\ \eta_{j,k}^s = 0\right) \Rightarrow (8) = 0.$$

$$(7)\ \left(x_j^t > x_j^k,\ x_j^s \leq x_j^{k+1}\right) \Rightarrow \left(\eta_{j,k}^t = 0,\ \eta_{j,k+1}^t = 0,\ \eta_{j,k}^s = 1\right) \Rightarrow (8) = L_j\left(x_j^k - x_j^{k+1}\right).$$

The total lean load in the kth interval is obtained by summing expression 8 over all the lean streams that may exist within interval k. The total rich load in the kth interval is represented by an expression analogous to that for the total lean load in this interval, and is equal to

$$\sum_{i=1}^{N_R} G_i[\lambda_{i,k}^s(y^{k+1} - y^k) - \lambda_{i,k}^t(y_i^t - y^k) + \lambda_{i,k+1}^t(y^t - y^{k+1})]. \tag{9}$$

Using the above expressions 8 and 9 for the total lean and rich loads in each interval, one can develop a mathematical representation of the first and second laws of thermodynamics, and subsequently a formulation of the variable target minimum utility cost mass-exchange network synthesis problem

$$\min \mu = \sum_{j=1}^{N_S} c_j L_j \tag{10}$$

s.t.

$$\delta_k + \sum_{i=1}^{N_R} G_i[\lambda_{i,k+1}^t(y^{k+1} - y^k) - \lambda_{i,k}^t(y_i^t - y^k) + \lambda_{i,k+1}^t(y^t - y^{k+1})] - \sum_{j=1}^{N_S} L_j[\eta_{j,k}^s(x_j^k - x_j^{k+1}) + \eta_{j,k}^t(x_j^t - x_j^k) - \eta_{j,k+1}^t(x_j^t - x_j^{k+1})] - \delta_{k+1} = 0, \quad k = 1,\ldots,N_{\text{int}}, \tag{11}$$

$$(2\lambda_{i,k}^t - 1)(y^k - y_i^t) \geq 0,\ i = 1,\ldots,N_R,\ k = 1,\ldots,N_{\text{int}} + 1 \tag{12}$$

$$\left(2\eta_{j,k}^t - 1\right)\left(x_j^k - x_j^t\right) \geq 0,\ j = 1,\ldots,N_S,\ k = 1,\ldots,N_{\text{int}} + 1 \tag{13}$$

$$\lambda_{i,k}^t(\lambda_{i,k}^t - 1) = 0,\ i = 1,\ldots,N_R,\ k = 1,\ldots,N_{\text{int}} + 1 \tag{14}$$

$$\eta_{j,k}^t\left(\eta_{j,k}^t - 1\right) = 0,\ j = 1,\ldots,N_S,\ k = 1,\ldots,N_{\text{int}} + 1 \tag{15}$$

$$y_i^u \geq y_i^t \geq y_i^l,\ i = 1,\ldots,N_R, \tag{16}$$

$$L_j^l \leq L_j \leq L_j^u,\ j = 1,\ldots,N_S, \tag{17}$$

$$x_j^l \leq x_j^t \leq x_j^u,\ j = 1,\ldots,N_S, \tag{18}$$

$$\delta_k \geq 0, \qquad k = 2,\ldots,N_{\text{int}}, \tag{19}$$

$$\delta_1 = \delta_{N_{\text{int}}+1} = 0. \tag{20}$$

This problem is a mixed integer nonlinear program (MINLP), as several terms, such as $G_i\lambda_{i,k}^s(y^{k+1} - y^k)$ in Eqs. 11, involve the products of two or more variables, some of which are integers. The optimization vector for the problem is $v^T \triangleq [y_1^t,\ \lambda_{1,1}^t \cdots \lambda_{1,N_{\text{int}}+1}^t, \cdots y_{N_R}^t,\ \lambda_{N_R,1}^t \cdots \lambda_{N_R,N_{\text{int}}+1}^t,\ x_1^t,\ \eta_{1,1}^t \cdots \eta_{1,N_{\text{int}}+1}^t,\ L_1 \cdots x_{N_S}^t,\ \eta_{N_S,1}^t \cdots \eta_{N_S,N_{\text{int}}+1}^t,\ L_{N_S},\ \delta_1 \cdots \delta_{N_{\text{int}}+1},\ \mu]$.

In the above formulation, Eqs. 11 represent the total mass exchanged within the kth interval. The first term, δ_k, in each of these N_{int} equations is the residual mass load delivered to the kth interval from the intervals above it, the next term is the total rich load in this interval, followed by the total lean load in the interval, and the residual mass load forwarded to the $(k+1)$th interval below δ_{k+1}. Inequalities 12 and 13 and Eqs. 14 and 15 stem from the definition of the binary variables $\lambda_{i,k}^t$ and $\eta_{j,k}^t$. Inequalities 16–18 define bounds on the flow and composition variables. These bounds are set by external resource limitations (such as the lean stream availability). Inequalities 19 state the second law of thermodynamics by requiring that the residual mass δ_{k+1} from the kth interval can only be transferred to the interval below it. Equation 20 states that there is neither mass load entering the CID above interval 1, nor any mass leaving the CID from the last interval. The total mass balance would thus be satisfied.

In Gupta and Manousiouthakis (1993), we had presented an algorithm to determine the global optimum of a similar MINLP. First, the mixed integer nonlinear constraints were transformed into nonlinear constraints, thus converting the MINLP into a NLP with polynomial constraints. Several properties were then developed that helped restrict the search space for the optimum solution. Finally, an algorithm to determine the *global* optimum of such an NLP was presented. The same algorithm can be used to solve the MINLP proposed here. However, for problems with several rich and lean streams, both MINLP formulations require large computational times for global solution.

An alternative LP formulation for the variable target MEN synthesis problem is proposed below. The advantage of this formulation is that solution of even a large LP requires little computational effort.

LP formulation

Let us consider the same CID as the one employed earlier, with a total of N_{int} intervals, counted from the top to the bottom of the CID. Using this CID, we propose a fixed target MEN synthesis problem, with special characteristics, that is shown to be equivalent to the variable target MEN synthesis problem.

First, binary variables associated with the upper bounds on the target compositions of the rich and lean streams, x_j^u or y_i^u, are defined as follows

$$\lambda_{i,k}^{u} \triangleq \begin{cases} 1 \text{ if } y_i^u < y^k & i=1,\ldots,N_R \\ 0 \text{ if } y_i^u \geq y^k & k=1,\ldots,N_{\text{int}}+1, \end{cases}$$

$$\eta_{j,k}^{u} \triangleq \begin{cases} 1 \text{ if } x_j^u < x_j^k & j=1,\ldots,N_S \\ 0 \text{ if } x_j^u \geq x_j^k & k=1,\ldots,N_{\text{int}}+1, \end{cases}$$

For any lean stream S_j, it then holds that $\eta_{j,k}^s \geq \eta_{j,k}^u$. Similarly, for any rich stream R_i, it holds that $\lambda_{i,k}^l \geq \lambda_{i,k}^s$. Binary variables are also defined to position the streams with respect to the lower bounds on their target compositions

$$\lambda_{i,k}^{l} \triangleq \begin{cases} 1 \text{ if } y_i^l < y^k & i=1,\ldots,N_R \\ 0 \text{ if } y_i^l \geq y^k & k=1,\ldots,N_{\text{int}}+1, \end{cases}$$

$$\eta_{j,k}^{l} \triangleq \begin{cases} 1 \text{ if } x_j^l < x_j^k & j=1,\ldots,N_S \\ 0 \text{ if } x_j^l \geq x_j^k & k=1,\ldots,N_{\text{int}}+1, \end{cases}$$

One should note that all the binary variables $\lambda_{i,k}^u$, $\lambda_{i,k}^l$, $\lambda_{i,k}^s$, $\eta_{j,k}^u$, $\eta_{j,k}^l$, and $\eta_{j,k}^s$, are fixed once the problem is specified.

Consider now a lean stream S_j and a set of substreams $S_{j,k}$, one substream for each interval in the CID, $k=1,\ldots,N_{\text{int}}$ and $j=1,\ldots,N_S$. Stream $S_{j,k}$ exists only in the kth interval, and may be thought of as having a supply composition x_j^{k+1} and a fixed target composition x_j^k. Associated with any jth set of substreams $S_{j,k}$, $k=1,\ldots,N_{\text{int}}$, is a supply composition x_j^s, and upper and lower bounds on the stream target composition x_j^u and x_j^l as defined above for stream S_j. The load for the stream $S_{j,k}$ in the kth interval is

$$L_{j,k}(\eta_{j,k}^s - \eta_{j,k}^u)\left(x_j^k - x_j^{k+1}\right), \tag{21}$$

while the load for the stream $S_{j,k}$ in the lth interval ($l \neq k$) is zero. The kth interval load should be positive and nonzero for any stream $S_{j,k}$ that has $L_{j,k} > 0$, $x_j^u \geq x_j^k$, and $x_j^s \leq x_j^{k+1}$. The validity of expression 21 for the various possible locations of $S_{j,k}$ with respect to x_j^s and x_j^u (see Figure 4) is established below

$$(1)\ \left(x_j^u \leq x_j^{k+1}\right) \Rightarrow (\eta_{j,k}^u = 1,\ \eta_{j,k}^s = 1) \Rightarrow (21) = 0.$$

The compositions x_j^s and x_j^u are, by definition of the CID, the same as one of the x_j^m compositions, and hence, cannot be between x_j^k and x_j^{k+1}. If $x_j^s = x_j^m$ or $x_j^u = x_j^m$, for any m, x_j^s or x_j^u is replaced by x_j^m.

$$(2)\ \left(x_j^u \geq x_j^k,\ x_j^s \leq x_j^{k+1}\right) \Rightarrow (\eta_{j,k}^u = 0,\ \eta_{j,k}^s = 1) \Rightarrow (21) = L_{j,k}\left(x_j^k - x_j^{k+1}\right).$$

$$(3)\ \left(x_j^u = x_j^k,\ x_j^s = x_j^k\right) \Rightarrow (\eta_{j,k}^u = 0,\ \eta_{j,k}^s = 0) \Rightarrow (21) = 0.$$

$$(4)\ \left(x_j^u > x_j^k,\ x_j^s \geq x_j^k\right) \Rightarrow (\eta_{j,k}^u = 0,\ \eta_{j,k}^s = 0) \Rightarrow (21) = 0.$$

Similarly, for any rich stream R_i a set of substreams $R_{i,k}$, $j=1,\ldots,N_R$, $k=1,\ldots,N_{\text{int}}$ is considered. Substream $R_{i,k}$ exists only in the kth interval, and may be thought of as having a supply composition y^k and a target composition y^{k+1}. Associated with the ith rich substream set is the supply composition y_i^s and upper and lower bounds on the target composition y_i^u and y_i^l from the stream R_i. In analogy to expression 21, the rich load for stream $R_{i,k}$ in the kth interval is

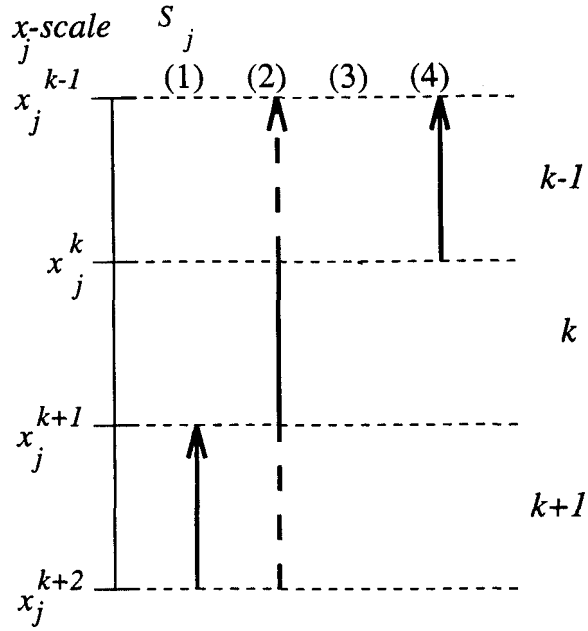

Figure 4. CID showing possible locations of the supply and upper bound on target compositions of stream, S_j, x_j^s and x_j^u, respectively, with respect to x_j^k.

Each interval has associated with it the substream $S_{j,k}$.

$$G_{i,k}(\lambda_{i,k}^l - \lambda_{i,k}^s)(y^k - y^{k+1}), \tag{22}$$

while the load for the stream $R_{i,k}$ in the lth interval ($l \neq k$) is zero. The kth interval load is positive and nonzero for any stream $R_{i,k}$ that has $G_{i,k} > 0$, $y_i^s \geq y^k$, and $y_j^l \leq y^{k+1}$. Here, y_i^l is employed because the maximal span of stream R_i can be from y_i^s to y_i^l.

The resulting linear problem formulation is

$$\min \nu = \sum_{j=1}^{N_S} c_j L_{j,N_{\text{int}}} \tag{23}$$

s.t.

$$\delta_k + \sum_{i=1}^{N_R} G_{i,k}(\lambda_{i,k}^l - \lambda_{i,k}^s)(y^k - y^{k+1}) - \sum_{j=1}^{N_S} L_{j,k}(\eta_{j,k}^s - \eta_{j,k}^u)\left(x_j^k - x_j^{k+1}\right) - \delta_{k+1} = 0, \quad k=1,\ldots,N_{\text{int}}, \tag{24}$$

$$G_{i,k-1} \geq G_{i,k} \geq 0,\ i=2,\ldots,N_R,\ k=1,\ldots,N_{\text{int}} \tag{25}$$

$$0 \leq L_{j,k-1} \leq L_{j,k},\ j=1,\ldots,N_S,\ k=2,\ldots,N_{\text{int}} \tag{26}$$

$$G_{i,1} = G_i,\ i=1,\ldots,N_R, \tag{27}$$

$$\lambda^u_{i,k}(G_{i,k-1}-G_{i,k})=0,\ i=1,\ldots,N_R,\ k=2,\ldots,N_{\text{int}} \quad (28)$$

$$\left(1-\eta^l_{j,k}\right)(L_{j,k}-L_{j,k+1})=0,\ j=1,\ldots,N_S,\quad k=1,\ldots,N_{\text{int}}-1 \quad (29)$$

$$L^l_j \le L_{j,N_{\text{int}}} \le L^u_j,\ j=1,\ldots,N_S, \quad (30)$$

$$\delta_k \ge 0, \qquad k=2,\ldots,N_{\text{int}}, \quad (31)$$

$$\delta_1=\delta_{N_{\text{int}}+1}=0, \quad (32)$$

For this problem, define a vector that is constituted by the problem variables $w^T \triangleq [L_{1,1}\cdots L_{1,N_{\text{int}}}\cdots L_{N_S,1}\cdots L_{N_S,N_{\text{int}}},\ G_{1,2}\cdots G_{1,N_{\text{int}}}\cdots G_{N_R,2}\cdots G_{N_R,N_{\text{int}}},\ \delta_1\cdots\delta_{N_{\text{int}}+1},\ v]$.

In the above formulation, Eqs. 24 represent the total mass exchanged within the kth interval. In these equations, the first term is the residual mass load delivered to the kth interval from the intervals above it. The next term is the total rich load in this interval, followed by the total lean load in the interval, and the residual mass load forwarded to the $(k+1)$th interval below the kth interval δ_{k+1}. Note that both Eqs. 11 and 24 are the first law balances around each of the same N_{int} intervals.

Inequalities 25 require that the flow rate of each *rich* substream in the kth interval $G_{i,k}$ be less than or equal to the flow rate of the substream due to the same stream in the $(k-1)$th interval *above* it, $G_{i,k-1}$. Similarly, inequalities 26 require that the flow rate of each *lean* substream in the $(k-1)$th interval $L_{j,k-1}$ be less than or equal to the flow rate of the substream due to the same stream in the kth interval *below* it $L_{j,k}$. These inequalities are required to ensure the equivalence of the LP and the MINP (see next section).

Equations 27 set the flow rate of every rich substream in the first interval to the value specified in the problem definition. Equations 28 state that the flow rate of the substreams corresponding to rich stream R_i and intervals above y^u_i are identical. This constraint ensures the upper bound requirement on the target composition of R_i is met, and holds only for $k=1,\ldots,N_{\text{int}}+1$ such that $y^k \ge y^u_i$ since the corresponding $\lambda^u_{i,k}=1$. It is likely that some rich stream R_i will have $y^s_i < y^1$. If n_i is defined such that $y^{n_i}=y^s_i$, constraints 28 and 27 ensure that $G_i=G_{i,k}$, $k=1,\ldots,n_i$. Moreover, due to expression 22 the rich load in these intervals, due to $R_{i,k}$, is zero.

Similarly, Eqs. 29 state that the flow rates of every lean substream corresponding to the jth lean stream and existing in intervals below x^l_j are identical. This constraint ensures that the required lower bound on the target of the lean stream is met, and it holds for $x^k_j \le x^l_j$. The flow rates of substreams $S_{i,k}=S_{i,N_{\text{int}}}$ for $k=m_j-1,\ldots,N_{\text{int}}$, where m_j is chosen such that $x^{m_j}_j=x^s_j$. Again due to Expression 21 the lean load in these intervals due to $S_{j,k}$ is nil.

Inequalities 30 bound the lean stream flow rate $L_j=L_{m,N_{\text{int}}}$ based on the problem specification, such as the lean stream availability. Inequalities 31 state the second law of thermodynamics by requiring that the residual mass δ_{k+1} from the kth interval can only be transferred to the interval below it. Equation 32 states that there is neither mass load entering the CID above interval 1, nor any mass leaving the CID from the last interval. The total mass balance would thus be satisfied.

The objective function of problem 23 should involve only the bottom-most substream (from x^s_j), S_{i,m_i-1}, where m_j is defined such that $x^{m_j}_j=x^s_j$, since it has the highest flow rate of all substreams for S_j. Due to constraints 29 and the definition of $\eta^l_{j,k}$, we have $L_{i,m_j-1}=L_{i,N_{\text{int}}}$, where the latter replaces L_{i,m_j-1} in the objective.

Note that for every set of lean substreams featured in problem 23, constraint 29 forces the flow rates of the substreams from the bottom-most interval above the supply composition to the last interval to be identical. This has been done only to simplify the notation, since constraint 24 ensures that the load due to the substreams associated with S_j in intervals below x^s_j is nil. Similarly, constraints 24 also ensure that the load due to the substreams associated with S_j in intervals above x^u_j is nil, and these substreams are included in the formulation to simplify the notation as well.

In the next section, a theorem is proven to establish that the optimal solution for problem 10 can lead to a feasible solution for problem 23, and vice versa. Hence, the nonlinear problem has an equivalent linear formulation.

Equivalence of MINLP and LP Formulations

First, the following fact establishes that any lean stream with a nonzero optimal flow rate in the optimum solution to problem 10 exists at or above the top edge of the interval whose lower edge is the supply composition of this stream. The superscript * is employed below to indicate the optimal value of any variable.

Fact 1. Consider an optimum solution v^* for problem 10. Any lean stream that has a nonzero optimal flow rate L^*_j in v^* must have an optimum target composition x^{t*}_j that is at or above the upper edge of the interval whose lower edge is the supply composition of this stream. Mathematically, for every $j \in \{1,\ldots,N_S\}$ that has $L^*_j>0$, it holds that $x^{t*}_j \ge x^{m_j-1}_j$ for every $j \in \{1,\ldots,N_S\}$ that has $L^*_j>0$, where m_j is defined such that $x^{m_j}_j=x^s_j$.

Proof. Consider $j \in \{1,\ldots,N_S\}$ such that $L^*_j>0$. There are two possibilities $x^l_j > x^s_j$, or $x^l_j=x^s_j$. For the first case, since $x^l_j>x^s_j$ and x^l_j and x^s_j define the top edges of two different intervals on the CID, therefore, $x^{t*}_j \ge x^l_j \ge x^{m_j-1}_j$.

For the second case, when $x^l_j=x^s_j$, to establish that $x^{t*}_j \ge x^{m_j-1}_j$, assume that the optimum target composition at the minimum utility cost solution lies strictly in the interval whose lower edge is the supply composition of this stream, i.e., $x^s_j < x^{t*}_j < x^{m_j-1}_j$. While keeping all other variables in v^* constant, replace x^{t*}_j with $x^t_j \triangleq x^{m_j-1}_j$, and L^*_j with

$$L_j \triangleq \frac{x^{t*}_j-x^s_j}{x^{m_j-1}_j-x^s_j}L^*_j. \quad (33)$$

Since all the other stream flow rates and target compositions are unaltered, δ^*_k, $k=1,\ldots,m_j-1$ are unchanged due to this substitution. The lean load due to S_j in the (m_j-1)th interval of the CID is also unaltered by this change

$$L^*_j\left(x^{t*}_j-x^s_j\right)=\frac{x^{t*}_j-x^s_j}{x^{m_j-1}_j-x^s_j}L^*_j\left(x^{m_j-1}_j-x^s_j\right)$$

$$=L_j\left(x^{m_j-1}_j-x^s_j\right).$$

As no other stream flow rates or target compositions were altered, this change does not affect $\delta^*_{m_j}$, and therefore, δ^*_k, $k = m_j + 1, \ldots, N_{\text{int}} + 1$. Thus, a new feasible point has been obtained for problem 10, with $\sum_{m=1, m \neq j}^{N-S} c_m L^*_m + c_j L_j = \mu < \mu^*$, since $L_j < L^*_j$. Hence, v^* was not the minimum utility cost solution, leading to a contradiction. O.E.Δ. ■

The equivalence of the two problems, Eqs. 10 and 23, is established in the following theorem.

Theorem 1. Optimization problems 10 and 23 are equivalent. Mathematically, $\nu^* = \mu^*$.

Proof. The proof is given in Appendix A.

Remark 1. One can develop an alternative LP formulation for problem 23 by replacing the lean streams in problem 10 with sets of *parallel* lean substreams $S'_{j,k}$ that have an inlet composition x^s_j, and an outlet composition x^k_j. In contrast, problem 23 employs *sequential* lean substreams that have an inlet composition x^{k+1}_j, and an outlet composition x^k_j. The representation of lean streams in the MINLP, LP and this alternative formulation are shown in Figure 5.

The flow rates of these new parallel substreams $L'_{j,k}$ are related to those of the sequential substreams $L_{j,k}$ as

$$L'_{j,k} = L_{j,k} - L_{j,k-1}. \tag{34}$$

This relation implies that the formulation in problem 23 can itself be employed if $L_{j,k}$ are replaced with $L'_{j,k}$. The flow rates $L'_{j,k}$ can be calculated from w by employing Eq. 34.

Remark 2. It should also be noted that one does not need to create substreams for all the intervals in problem 23. As mentioned earlier, only stream inlets can be pinch point candidates. Hence, the LP formulation size can be decreased by creating the substreams only across pinch point candidates, instead of creating substreams for every interval of the CID.

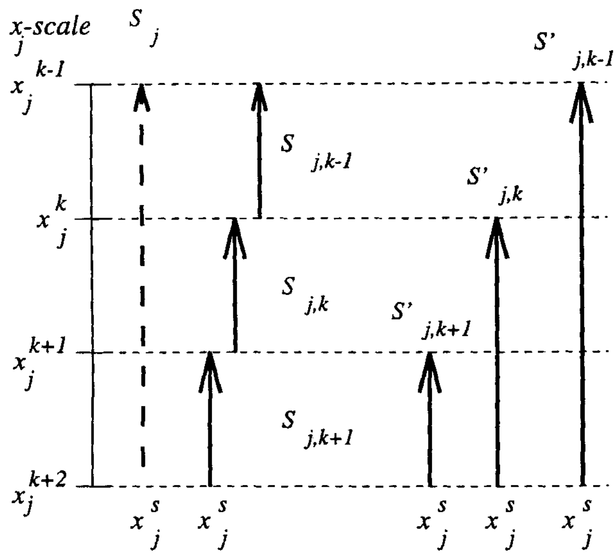

Figure 5. CID showing three different representations for stream S_j.

The first stream is S_j employed in the MINLP formulation, and its target can be anywhere in the range shown as a dotted line. Next is a set of sequential substreams, employed in the LP formulation. The third representation is a set of parallel substreams that may be employed in an alternative LP formulation.

Table 1. Stream Data for Example 1*

	Rich Streams				Lean Streams		
	G_i kg/s	y^s_i kg/kg	y^u_i kg/kg		x^s_j kg/kg	x^u_j kg/kg	c_j \$/kg
R_1	0.1	0.045	0.02	S_1	0.0015	0.075	0.7
R_2	1.5	0.03	0.001	S_2	0.004	0.05	0.03

*$y^l_i = y^u_i$, and $x^l_j = x^s_j$.

In the following section, the LP problem formulation is employed to solve two case studies in hazardous waste minimization. The first is based on a metal pickling plant, and the second one is based on a plastics manufacturing plant.

Example Problems

Example 1

This problem features two rich and two lean streams. The waste minimization task is to recover zinc chloride from the effluent of a metal pickling plant. Details on the process have been published by Parthasaradhy (1989); El-Halwagi and Manousiouthakis (1990a); Lo et al., (1983); Gupta and Manousiouthakis (1993). The data for this example are presented in Table 1. The two effluent streams from the plant are the spent pickle liquor R_1, and the rinse wastewater R_2. The lean streams are a strong-base ion-exchange resin S_1 and the extraction solvent, tributyl phosphate S_2. The lean stream target compositions can vary between this supply and upper bound compositions. The rich stream target compositions are fixed. Linear equilibrium relations that depend only on the solute-solvent system are considered

$$(S1) \qquad y = 0.376(x_1 + \epsilon) + 0.0001$$
$$(S2) \qquad y = 0.845(x_2 + \epsilon)$$

with $\epsilon = 0.0001$.With these data, a composition interval diagram (CID), as shown in Figure 6, is constructed.

Let us first solve the variable target MEN synthesis problem using the ranges given in Table 1. The CID drawn for this example has seven intervals. Since the rich streams have fixed targets ($y^l_i = y^u_i$), constraints 28 imply that $G_{i,k-1} = G_{i,k} = G_i$ $k = 1, \ldots, 7$. Stream S_1 is decomposed into four substreams with unknown flow rates: $L_{1,4}$, $L_{1,5}$, $L_{1,6}$, and $L_{1,7}$. Similarly, stream S_2 is decomposed into four substreams with unknown flow rates: $L_{2,2}$, $L_{2,3}$, $L_{2,4}$, and $L_{2,5}$. The solution involves the variables: [$L_{1,4}$, $L_{1,5}$, $L_{1,6}$, $L_{1,7}$, $L_{2,2}$, $L_{2,3}$, $L_{2,4}$, $L_{2,5}$, δ_3, δ_4, δ_5, δ_6, δ_7, ν], and is: [0.503087, 0.503087, 0.503087, 0.503087, 0.102761, 0.239568, 0.239568, 0.239568, 0.0, 0.002189, 0.002009, 0.0, 0.000399, 0.35935]. Since $\delta^*_3 = \delta^*_6 = 0.0$, the two pinch points are: $y^3 = 0.03$ and $y^6 = 0.003465$. From this solution, employing Theorem 1, the solution of the MINLP can be constructed. It is: $L_1 = 0.503087$ kg/s, $L_2 = 0.239568$ kg/s with a minimum utility cost of \$0.3594/s. While $x^t_1 = x^u_1$, x^t_2 is determined from Eq. 53: $x^t_2 = 0.102761\ (0.05 - 0.035403)/0.239568 + 0.035403 = 0.04166$ kg/kg, and is less than $x^u_2 = 0.05$ kg/kg.

To compare the savings due to variable targets, the fixed target problem is solved by forcing the outlet compositions of

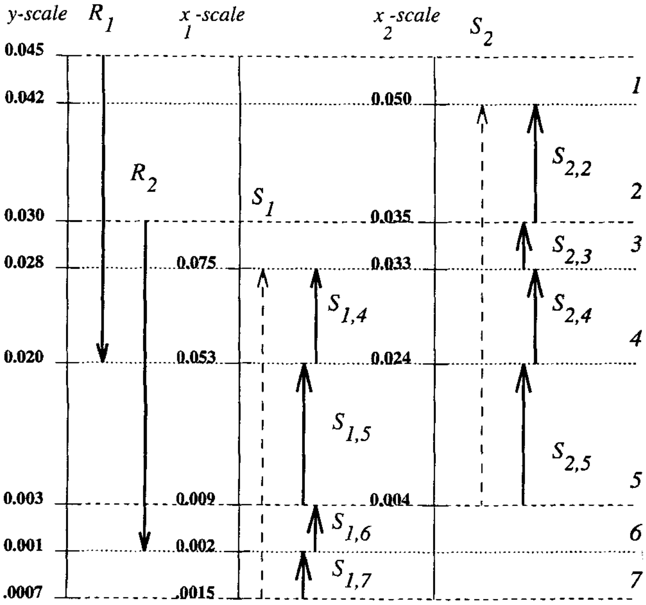

Figure 6. CID diagram for example 1 (not to scale).

Streams S_1 and S_2 have been replaced by their corresponding substreams.

the lean streams to be at their upper bound. This optimization program has the solution $L_1 = 0.5615$ kg/s and $L_2 = 0.1028$ kg/s. Notice that if stream S_2 is forced to exit at $x_2^t = 0.05$, the maximum feasible flow rate for S_2 is 0.1028 kg/s. This stream is the cheaper of the two, but it cannot be used to accommodate the entire rich load. Hence, the utility cost for the fixed target problem at \$0.396/s is not the lowest that can be obtained for this network. The result for the variable target problem shows that S_1 is used only to render the mass exchange from the lowest rich intervals (intervals 6 and 7 on the CID) feasible. Once this S_1 is utilized for its entire mass-exchange capacity, the remaining rich load is removed by the cheaper solvent S_2. This accounts for the 9.2% savings in the utility cost obtained with variable targets on the stream outlet compositions.

The MINLP formulation for the variable target problem was convexified and solved as a series of convex NLPs employing the algorithm outlined in Gupta and Manousiouthakis (1993). A standard nonlinear solver MINOS (Murtagh and Saunders, 1987) was used to solve the convex NLPs for the MINLP formulation. The MINLP was solved in approximately 90 s of CPU time on an Apollo 10000. The linear program proposed here was solved with the same nonlinear solver MINOS in only 0.4 CPU s, underscoring the computational advantage of an LP. The larger the MEN synthesis problem, the more the time savings will be for the LP formulation.

Example 2

Acrolein is a polar-organic pollutant listed on the Priority Pollutants list of the U.S. Environmental Protection Agency (Wise and Fahrenthold, 1981). Acrolein is manufactured from propylene in petrochemical plants. It is utilized as a monomer for the manufacture of acrylic resins (latex), allyl alcohol, and methylethyl ketone. Water is contaminated with acrolein in these plants because it is either a reaction byproduct, or is required for mass-exchange operations, or is used for heating (steam) and cooling (Joshi, 1983). Thus, wastewaters from such petrochemical plants that manufacture acrolein, acrylic resins, alkyd resins, allyl alcohol, methylethyl ketone, and vinyl acetate would contain acrolein (Wise and Fahrenthold, 1981).

The design task is to remove acrolein from the wastewater effluents of a plastics synthesis plant.

The various rich and lean streams are:

R_1: Acrolein containing wastewater
R_2: Acrolein containing wastewater
S_1: Methyl Isobutyl Ketone
S_2: Butyl Acetate
S_3: Toluene
S_4: Wastewater with no acrolein.

The data for this example are presented in Table 2.

Linear equilibrium relations, independent of the solute-solvent system are employed (Joshi et al., 1984)

$$(S1) \qquad y = 0.2041(x_1 + \epsilon)$$
$$(S2) \qquad y = 0.3846(x_2 + \epsilon)$$
$$(S3) \qquad y = 0.4545(x_3 + \epsilon)$$
$$(S4) \qquad y = 1.0x_4$$

with $\epsilon = 1.0 \times 10^{-7}$ kg/kg. Relation $S4$ involves identical solvents, i.e., wastewater, hence is equivalent to $y = x_4$. Further details on the equilibrium relations and possible lean solvents that can be used for this separation task are available (Joshi, 1983; Joshi et al., 1984).

A composition interval diagram (CID) is constructed from the above data, and is shown in Figure 7. There are ten intervals in the CID. The rich streams have fixed target compositions.

Table 2. Stream Data for Effluent Streams in a Typical Acrolein Plant and for Available MSAs*

	Rich Streams				Lean Streams			
	G_i kg/s	y_i^s kg/kg	y_i^u kg/kg		c_j \$/kg	L_j^u kg/s	x_j^s kg/kg	x_j^u kg/kg
R_1	14.805	0.0002	0.000002	S_1	0.061	—	0.000005	0.0085
R_2	6.75	0.0018	0.000005	S_2	0.05	—	0.000001	0.000975
				S_3	0.019	—	0.00002	0.0002
				S_4	0.0	68.0	0.0	0.000005

*S_1, S_2 and S_3 are methyl isobutyl ketone, butyl acetate and toluene, respectively; S_4 is a wastewater stream that is free of acrolein. Here, $y_i^l = y_i^u$, and $x_j^l = x_j^s$.

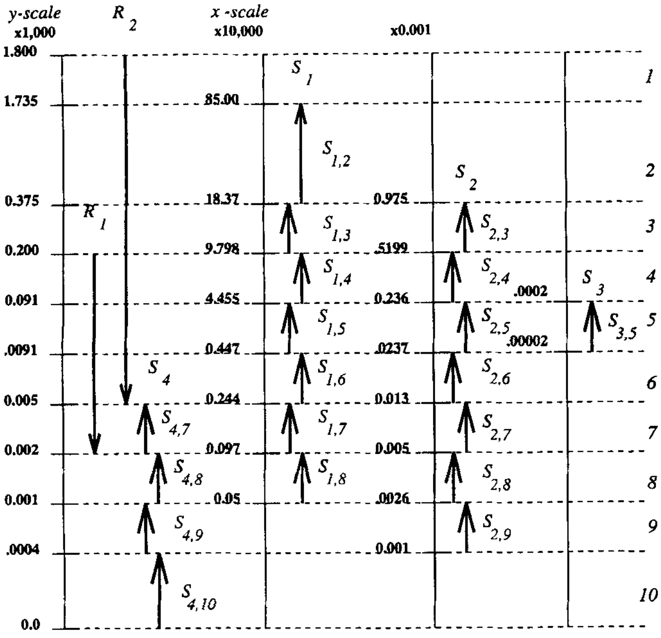

Figure 7. CID diagram for example 2 (not to scale).

The lean streams have been replaced by their corresponding substreams, and are not shown themselves.

Consider, first the variable target MEN synthesis problem. The problem formulation (problem 23) is

$$\min \nu = 0.061 L_{1,8} + 0.05 L_{2,9} + 0.019 L_{3,5} \tag{35}$$

s.t.

$$6.75 \Delta y^1 - \delta_2 = 0, \tag{36}$$

$$4.3962 \times 10^{-4} + 6.75 \Delta y^2 - L_{1,2} \Delta x_1^2 - \delta_3 = 0, \tag{37}$$

$$\delta_3 + 6.75 \Delta y^3 - L_{1,3} \Delta x_1^3 - L_{2,3} \Delta x_2^3 - \delta_4 = 0, \tag{38}$$

$$\delta_4 + (14.805 + 6.75) \Delta y^4 - L_{1,4} \Delta x_1^4 - L_{2,4} \Delta x_2^4 - \delta_5 = 0, \tag{39}$$

$$\delta_5 + 21.555 \Delta y^5 - L_{1,5} \Delta x_1^5 - L_{2,5} \Delta x_2^5 - L_{3,5} \Delta x_3^5 - \delta_6 = 0, \tag{40}$$

$$\delta_6 + 21.555 \Delta y^6 - L_{1,6} \Delta x_1^6 - L_{2,6} \Delta x_2^6 - \delta_7 = 0, \tag{41}$$

$$\delta_7 + 14.805 \Delta y^7 - L_{1,7} \Delta x_1^7 - L_{2,7} \Delta x_2^7 - L_{4,7} \Delta x_4^7 - \delta_8 = 0, \tag{42}$$

$$\delta_8 - L_{1,8} \Delta x_1^8 - L_{2,8} \Delta x_2^8 - L_{4,8} \Delta x_4^8 - \delta_9 = 0, \tag{43}$$

$$\delta_9 - L_{2,9} \Delta x_2^9 - L_{4,9} \Delta x_4^9 - \delta_{10} = 0, \tag{44}$$

$$\delta_{10} - L_{4,10} \Delta x_4^{10} = 0, \tag{45}$$

$$0 \le L_{1,2} \le L_{1,3} \le L_{1,4} \le L_{1,5} \le L_{1,6} \le L_{1,7} \le L_{1,8}, \tag{46}$$

$$0 \le L_{2,3} \le L_{2,4} \le L_{2,5} \le L_{2,6} \le L_{2,7} \le L_{2,8} \le L_{2,9}, \tag{47}$$

$$0 \le L_{4,7} \le L_{4,8} \le L_{4,9} \le L_{4,10} \le 68.0, \tag{48}$$

$$\delta_k \ge 0, \quad k = 2, \ldots, 10, \tag{49}$$

where, for clarity, variables that are not free have not been shown, and some terms have been replaced by the definitions: $\Delta x_j^k \triangleq x_j^k - x_j^{k+1}$ and $\Delta y^k \triangleq y^k - y^{k+1}$, all of which are known quantities.

Table 3. Variable Values for the Optimal Solution of Example 2

Variable	Value	Variable	Value	Variable	Value
$L_{1,2}^*$	1.436134	$L_{2,6}^*$	0.0	δ_2^*	4.3962×10^{-4}
$L_{1,3}^*$	1.436134	$L_{2,7}^*$	0.0	δ_3^*	5.0131×10^{-5}
$L_{1,4}^*$	4.008610	$L_{2,8}^*$	0.0	δ_4^*	0.0
$L_{1,5}^*$	4.008610	$L_{2,9}^*$	0.0	δ_5^*	2.0879×10^{-4}
$L_{1,6}^*$	4.008610	$L_{3,5}^*$	0.0	δ_6^*	3.6543×10^{-4}
$L_{1,7}^*$	4.008610	$L_{4,7}^*$	68.0	δ_7^*	3.7334×10^{-4}
$L_{1,8}^*$	4.008610	$L_{4,8}^*$	68.0	δ_8^*	1.5484×10^{-4}
$L_{2,3}^*$	0.0	$L_{4,9}^*$	68.0	δ_9^*	7.0782×10^{-5}
$L_{2,4}^*$	0.0	$L_{4,10}^*$	68.0	δ_{10}^*	2.8768×10^{-5}
$L_{2,5}^*$	0.0			ν^*	0.24452519

The optimal solution for this case study is shown in Table 3. With this solution, following the procedure in Theorem 1, a solution to problem 10 can be constructed. This minimum utility cost solution employs two of the four possible lean streams, S_1 with a flow rate of 4.0086 kg/s and S_4 with a flow rate of 68.0 kg/s. The wastewater stream S_4, available free of cost and existing in the low concentration range, is used to its maximum availability. The remaining rich load is taken up by methyl isobutyl ketone, which has the cheapest cost per unit of rich load absorbed since its allowable composition range spans three orders of magnitude. The maximum rich load exists in intervals where both R_1 and R_2 coexist, which occurs at $y^4 = y_1^s = 0.0002$. Since the rich load in intervals 1–3 is lesser, the optimal flow rates of substreams $L_{1,2}^* = L_{1,3}^* = 1.436134 < L_{1,4}^* = L_{1,8}^*$. Moreover, the transition takes place at y^4, which is the only pinch point in the solution ($\delta_4^* = 0.0$). Hence, the actual exit composition x_1^t is calculated to be $x_1^t = 1.436134(0.0085 - 0.000979812)/4.008610 + 0.000979812 = .003674$ kg/kg. The minimum utility cost for the MEN is \$0.2445/s.

Let us now consider the fixed target MEN synthesis problem for this example. When the target compositions of the lean stream are kept fixed at their upper bounds, the minimum utility cost is \$0.3523/s, and features three streams in the solution, with the flow rates: $L_1^* = 1.4361$ kg/s, $L_3^* = 13.9316$ kg/s, and $L_4^* = 68.0$ kg/s. The pinch point is still at the supply composition of R_1. The flow rate of S_1 here is identical to the flow rate of $S_{1,2}$ above, and establishes that the lower rich load above the pinch, in intervals 1–3, determines the maximum usage of S_1 in the fixed target situation. By allowing a higher flow rate of S_1, variable target compositions decrease the utility cost of the MEN by 30.6%.

Conclusions

The variable target mass-exchange network synthesis problem has been studied. In this problem, the target compositions of the streams, with respect to a single key component, are allowed to vary between upper and lower bounds. Many industrial MEN synthesis problems, such as in waste minimization, have a problem definition with variable targets. By reducing from their upper bounds, the outlet compositions of some lean streams, one may increase their feasibility for the overall MEN, and hence increase their mass-exchange capacity. This leads to a reduction in the minimum utility cost of the network. It may also allow greater recovery from the rich streams at no additional cost.

A novel linear programming formulation has been proposed to determine the minimum utility cost of a variable target MEN problem. An MINLP formulation is also proposed which is shown equivalent to the LP formulation.

It is also established that the equivalent MINLP and LP formulations have solutions that can be derived from one another. This result establishes that the MINLP can be solved as an LP, thus making it possible to synthesize MENs of industrial relevance involving several streams with variable targets.

Two hazardous waste minimization case studies are solved to illustrate the savings obtainable by having variable target compositions on the lean streams. These examples demonstrate that the linear program solution can be used to determine the MINLP solution, and that savings up to 30% in the operating cost of a mass-exchange network are possible if the outlet compositions of lean streams are allowed to vary.

It must also be pointed out that by simple analogy, the problem formulation presented here can be employed to determine the minimum utility (steam and cooling water, for example) cost of a heat-exchange network (HEN) with variable stream inlet and outlet temperatures. In an HEN, the hot streams correspond to the rich streams and the cold to the lean. There is a simple linear thermal equilibrium relationship $T_H = T_C + \Delta T_{\min}$. Inlet and outlet temperatures are variable if the HEN is synthesized as part of an entire process integration scheme. The formulation we have presented can be embedded into a flowsheet optimization procedure for determining what inlet and outlet temperatures and stream flow rates minimize the utility consumption of the process HEN. The implication of these results for standalone HENs is that the utility targets should be considered variable to obtain minimum utility consumption for the heat-exchange task.

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Notation

a_j = interval where x_j^t lies
b_j = intersection of the equilibrium line with x-axis
c_j = unit cost of lean stream S_j, /kg
G_i = mass-flow rate of rich stream R_i, kg/s
$G_{i,k}$ = mass-flow rate of rich substream $R_{i,k}$ in the kth interval, kg/s
L_j = mass-flow rate of lean stream S_j, kg/s
$L_{j,k}$ = mass-flow rate of lean substream $S_{j,k}$ in the kth interval, kg/s
m_j = slope of equilibrium line for lean stream S_j
N_{int} = number of intervals in the CID
N_R = number of rich streams in the network
N_S = number of lean streams in the network
p = index for pinch point candidate
x = mass fraction of key component in the lean stream, kg/kg
y = mass fraction of key component in the rich stream, kg/kg
w = problem variables for problem 23

Greek letters

δ_k = residual load entering interval k of the CID, kg/kg
ϵ = mass-transfer driving force or composition difference, kg/kg
$\eta_{j,k}$ = binary variable associated with lean stream S_j and interval k
$\lambda_{i,k}$ = binary variable associated with rich stream R_i and interval k
μ = objective value of problem 10
ν = objective value of problem 23

Subscripts

i = index for rich stream in the network
j = index for lean stream in the network
k = index for interval in the CID
m = index for interval in the CID
p = index for pinch point candidate

Superscripts

$*$ = optimal solution value
k = index for interval in the CID
l = lower bound of a variable
m = index for interval in the CID
p = pinch point candidate composition value
s = supply composition value
t = target composition value
u = upper bound of a variable

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Appendix: Proof of Theorem 1

$\mu^* \geq \nu^*$

Let the optimal solution to problem 10 be denoted by v^*, and consist of optimal lean stream flow rates L_j^*, the corresponding outlet compositions x_j^{t*}, optimal rich stream outlet compositions y_i^{t*}, optimal binary flags associated with the target compositions $\lambda_{i,k}^{t*}$ and $\eta_{j,k}^{t*}$, optimal residual loads δ_k^*, and the optimal objective value μ^*. We now consider two cases.

(1) If all the x_j^{t*} lie at the edge of an interval, i.e., for $j=1,\ldots,N_S$, $x_j^{t*}=x_j^{m_j}$, where $m_j \in \{1,\ldots,N_{\text{int}}+1\}$, and if all the y_i^{t*} also lie at the edge of an interval, i.e., for $i=1,\ldots,N_R$, $y_i^{t*}=y^{m_i}$, where $m_i \in \{1,\ldots,N_{\text{int}}+1\}$; then problem 23 has a feasible solution with $(0=L_{j,k},\ k=1,\ldots,m_j-1,\ 0\leq L_{j,k}=L_{j,N_{\text{int}}}=L_j^*,\ k=m_j,\ldots,N_{\text{int}};\ j=1,\ldots,N_S)$, $(G_{i,k}=G_i,\ k=1,\ldots,m_i-1,\ G_{i,k}=0,\ k=m_i,\ldots,N_{\text{int}};\ i=1,\ldots,N_R)$, and $\nu=\mu^*$. Since both the problem formulations involve identical component balances around the same intervals, the δ_k^* from v^* are identical to δ_k in w, $\forall k=1,\ldots,N_{\text{int}}+1$. Therefore, in this case $\nu=\mu^*$, and $\mu^*\geq\nu^*$.

(2) If some of the x_j^{t*} or y_i^{t*} do not lie at the edge of an interval, first, for all streams whose optimal target compositions lie at the edge of any interval, define substreams with flow rates as follows:

Lean Streams. Select $m_j \in \{1,\ldots,N_{\text{int}}+1\}$ such that $x_j^{m_j}=x_j^{t*}$, then let $(L_{j,k}=0,\ k=1,\ldots,m_j-1,\ 0\leq L_{j,k}=L_{j,N_{\text{int}}}=L_j^*,\ k=m_j,\ldots,N_{\text{int}})$.

Rich Streams. Select $m_i \in \{1,\ldots,N_{\text{int}}+1\}$ such that $y^{m_i}=y_i^{t*}$, then let $(G_{i,k}=G_i,\ k=1,\ldots,m_i-1,\ G_{i,k}=0,\ k=m_i,\ldots,N_{\text{int}})$.

Then proceed as follows: select the first interval from the top of the CID, say m, that has at least one lean or rich optimal target composition within it, i.e., $x_j^{m+1}<x_j^{t*}<x_j^m$; or $y^{m+1}<y_i^{t*}<y^m$.

For every lean stream S_j in the mth interval with $x_j^{m+1}<x_j^{t*}<x_j^m$, define a new substream $S_{j,m}$ with the inlet composition x_j^{m+1}, outlet composition x_j^m and flow rate

$$L_{j,m} \triangleq \frac{x_j^{t*}-x_j^{m+1}}{x_j^m-x_j^{m+1}}L_j^*. \quad \text{(A1)}$$

In each of the remaining intervals, define new substreams $S_{j,k}$ corresponding to stream S_j, with flow rates: $L_{j,k}=0$, $k=0,\ldots,m-1$, $L_{j,k}=L_j^*$, $k=m+1,\ldots,N_{\text{int}}$.

In an analogous fashion, for every rich stream that has a target composition y_i^{t*} with $y^{m+1}<y_i^{t*}<y^m$, in the same (mth) interval, define a new substream $R_{i,m}$ with the inlet composition y^m, outlet composition y^{m+1}, and flow rate

$$G_{i,m} \triangleq \frac{y^m-y_i^{t*}}{y^m-y^{m+1}}G_i. \quad \text{(A2)}$$

In each of the remaining intervals, define new substreams $R_{i,k}$ with the flow rates: $G_{i,k}=G_i$, $k=1,\ldots,m-1$, $G_{i,k}=0$, $k=m+1,\ldots,N_{\text{int}}$.

If constraint 24 is now written for $k=1,\ldots,m-1$, employing the $G_{i,k}$ and $L_{j,k}$ as defined above, then $\delta_k=\delta_k^*$ for $k=1,\ldots,m-1$, since the same intervals and rich and lean loads are employed in these constraints as in constraints 11 for problem 23. In the mth interval, the lean load due to $S_{j,m}$ and $R_{i,m}$ defined in Eqs. A1 and A2, is the same as that due to S_j and R_i, respectively, in constraint 11

$$L_j^*\left(x_j^{t*}-x_j^{m+1}\right)=\frac{x_j^{t*}-x_j^{m+1}}{x_j^m-x_j^{m+1}}L_j^*\left(x_j^m-x_j^{m+1}\right)$$
$$=L_{j,m}\left(x_j^m-x_j^{m+1}\right)$$

and

$$G_i(y^m-y_i^{t*})=\frac{y^m-y_i^{t*}}{y^m-y^{m+1}}G_i(y^m-y^{m+1})$$
$$=G_{i,m}(y^m-y^{m+1}).$$

Hence, $\delta_{m+1}=\delta_{m+1}^*$.

This procedure is repeated for the next lower interval that has any lean or rich optimal target composition within it, until the last interval. Since the rich and lean loads remain unaltered for these and perturbed intervals, and for any intervals in between, the definition of the vector w is complete. Note that due to this procedure and Fact 1, for $j=1,\ldots,N_S$, it holds that $L_{j,N_{\text{int}}}=L_{j,m_j}=L_j^*$, where m_j is the interval such that $x_j^s=x_j^{m_j+1}$. Hence, $\nu=\mu^*$.

Thus, a feasible point has been obtained for problem 23 from v^*, with

- $(L_{j,k}=0,\ k=1,\ldots,m_j-1,\ 0\leq L_{j,k}=L_{j,N_{\text{int}}}=L_j^*,\ k=m_j,\ldots,N_{\text{int}})$ for $j=1,\ldots,N_S$ such that $x_j^{t*}=x_j^{m_j}$, for some $m_j\in\{1,\ldots,N_{\text{int}}+1\}$;
- $(G_{i,k}=G_i,\ k=1,\ldots,m_i-1,\ G_{i,k}=0,\ k=m_i,\ldots,N_{\text{int}})$ for $i=1,\ldots,N_R$ such that $y_i^{t*}=y^{m_i}$, for some $m_i\in\{1,\ldots,N_{\text{int}}+1\}$;
- $L_{j,k}=0,\ k=0,\ldots,m_j-1,\ L_{j,k}=L_j^*,\ k=m_j+1,\ldots,N_{\text{int}}$, and L_{j,m_j} is

$$L_{j,m_j}=\frac{x_j^{t*}-x_j^{m_j+1}}{x_j^{m_j}-x_j^{m_j+1}}L_j^*,$$

for $j=1,\ldots,N_S$ such that $x_j^{m_j+1}<x_j^{t*}<x_j^{m_j}$, for some $m_j\in\{1,\ldots,N_{\text{int}}+1\}$;
- $G_{i,k}=G_i,\ k=1,\ldots,m_i-1,\ G_{i,k}=0,\ k=m_i+1,\ldots,N_{\text{int}}$, and G_{i,m_i} is

$$G_{i,m_i}=\frac{y^{m_i}-y_i^{t*}}{y^{m_i}-y^{m_i+1}}G_i,$$

for $i=1,\ldots,N_R$ such that $y^{m_i+1}<y_i^{t*}<y^{m_i}$, for some $m_i\in\{1,\ldots,N_{\text{int}}+1\}$;

- $\delta_k = \delta_k^*$ for $k = 1,\ldots,N_{\text{int}}+1$; and
- $\nu = \mu^*$.

Since for both cases it is established that $\nu = \mu^*$; it then holds that $\mu^* \geq \nu^*$.

$\boxed{\nu^* \geq \mu^*}$

To prove that problem 23 is an upper bound on problem 10, let the optimal solution to problem 23 be denoted by w^*, and let it consist of optimal lean substream flow rates $L_{j,k}^*$, optimal rich substream flow rates $G_{i,k}^*$, optimal residual loads δ_k^*, and the optimal objective value ν^*. Again, two cases are considered.

(1) First consider the case where all the substreams associated with a stream have an optimal flow rate in w^* that is either zero or the same nonzero value. For this case, for each set of lean substream flow rates, due to constraints 26 and 29, the top-most m_jth substream can be identified whose optimal flow rate is nonzero. If all the substreams associated with a lean stream have a zero optimal flow rate $m_j = N_{\text{int}}+1$. Similarly, for every rich substream set, identify the bottommost substream R_{i,m_i} such that $G_{i,m_i}^* > 0$. Then problem 10 has a feasible solution with ($L_j = L_{j,N_{\text{int}}}$, $x_j^t = x_j^{m_j}$, $j = 1,\ldots,N_S$), ($G_i = G_{i,1}$, $y_i^t = y^{m_i+1}$, $i = 1,\ldots,N_R$), and $\mu = \nu^*$. Since both the problem formulations involve identical component balances around the same intervals; and the loads due to substreams $S_{j,k}$ existing below x_j^s and substreams $R_{i,k}$ existing above y_i^s are zero, the δ_k^* from w^* are identical to δ_k in ν, $\forall k \in K$. Therefore, in this case, $\nu^* \geq \mu^*$.

(2) Next, consider the case where some of the optimal flow rates in a set of nonzero lean substreams are different. Then, to obtain a feasible solution from problem 23 for problem 10, replace the set of $S_{j,k}$, $k = 1,\ldots,N_{\text{int}}$ substreams by a stream with inlet composition x_j^s, a flow rate L_j defined as

$$L_j \triangleq L_{j,N_{\text{int}}}^*, \tag{A3}$$

and a target composition x_j^t defined as

$$x_j^t \triangleq \sum_{k=m_j}^{N_{\text{int}}} \frac{L_{j,k}^*}{L_{j,N_{\text{int}}}^*}(\eta_{j,k}^s - \eta_{j,k}^u)\left(x_j^k - x_j^{k+1}\right) + x_j^s, \tag{A4}$$

where the summation term in the righthand side of the above definition is the cumulative load of substreams associated with the jth stream, and m_j is the interval such that the exit composition of the topmost $S_{j,k}$ for which $L_{j,k}^* > 0$ is $x_j^{m_j}$. Then, for this m_jth interval it holds that $0 = L_{j,m_j-1}^* < L_{j,m_j}^*$, and

$$x_j^{m_j} = \sum_{k=m_j}^{N_{\text{int}}} (\eta_{j,k}^s - \eta_{j,k}^u)\left(x_j^k - x_j^{k+1}\right) + x_j^s. \tag{A5}$$

Since at least $L_{j,m_j}^* < L_{j,N_{\text{int}}}^*$, a comparison of Eq. A4 with Eq. A5 establishes that $x_j^{m_j} > x_j^t$.

For intervals $k = 0,\ldots,m_j - 1$, all the variables involved in the component balance around the interval stay the same, and, therefore, the residual load exiting the interval remains unaltered, i.e., $\delta_{k+1} = \delta_{k+1}^*$.

Now, let x_j^t lie in the a_jth interval, i.e., $x_j^{a_j} > x_j^t \geq x_j^{a_j+1}$. For intervals $k = m_j,\ldots,a_j-1$, the residual load leaving each interval has been augmented by the reduction in the lean load in that interval and in those above. Thus,

$$\delta_{k+1} = \delta_{k+1}^* + \sum_{i=m_j}^{k} L_{j,i}^*(\eta_{j,n}^s - \eta_{j,n}^u)\left(x_j^i - x_j^{i+1}\right). \tag{A6}$$

Since each of $L_{j,i}^*$, $(\eta_{j,n}^s - \eta_{j,n}^u)$, and $(x_j^i - x_j^{i+1})$ are positive quantities, $\delta_{k+1} \geq \delta_{k+1}^*$ for $k = m_j,\ldots,a_j - 1$.

For interval a_j, introduce

$$\delta_{a_j+1} = \delta_{a_j+1}^* + \sum_{k=m_j}^{a_j-1} L_{j,k}^*(\eta_{j,k}^s - \eta_{j,k}^u)\left(x_j^k - x_j^{k+1}\right) + L_{j,a_j}^*\left(x_j^{a_j} - x_j^t\right) - (L_j - L_{j,a_j}^*)\left(x_j^t - x_j^{a_j+1}\right) \tag{A7}$$

From Eq. A4

$$\begin{aligned} L_j\left(x_j^t - x_j^s\right) &= L_j\left(x^t - x_j^{a_j+1}\right) + \sum_{k=a_j+1}^{N_{\text{int}}} L_j(\eta_{j,k}^s - \eta_{j,k}^u)\left(x_j^k - x_j^{k+1}\right) \\ &= \sum_{k=m_j}^{N_{\text{int}}} L_{j,k}^*(\eta_{j,k}^s - \eta_{j,k}^u)\left(x_j^k - x_j^{k+1}\right) \\ &= \sum_{k=m_j}^{a_j-1} L_{j,k}^*(\eta_{j,k}^s - \eta_{j,k}^u)\left(x_j^k - x_j^{k+1}\right) + L_{j,a_j}^*\left(x_j^{a_j} - x_j^t\right) \quad \text{(A8)} \\ &\quad + L_{j,a_j}^*\left(x_j^t - x_j^{a_j+1}\right) + \sum_{k=a_j+1}^{N_{\text{int}}} L_{j,k}^*(\eta_{j,k}^s - \eta_{j,k}^u)\left(x_j^k - x_j^{k+1}\right), \end{aligned} \tag{A9}$$

Substituting Eq. A9 in Eq. A7, it holds

$$\delta_{a_j+1} = \delta_{a_j+1}^* + L_j\left(x_j^t - x_j^s\right) - \sum_{k=a_j+1}^{N_{\text{int}}} L_{j,k}^*(\eta_{j,k}^s - \eta_{j,k}^u)\left(x_j^k - x_j^{k+1}\right) - L_j\left(x_j^t - x_j^{a_j+1}\right)$$

Since $L_j \geq L_{j,k}^*$, from Eq. A8 we have

$$\sum_{k=a_j+1}^{N_{\text{int}}} L_{j,k}^*(\eta_{j,k}^s - \eta_{j,k}^u)\left(x_j^k - x_j^{k+1}\right) + L_j\left(x_j^t - x_j^{a_j+1}\right) \leq L_j\left(x_j^t - x_j^s\right).$$

Hence, $\delta_{a_j+1} \geq \delta_{a_j+1}^*$.

For intervals $k = a_j + 1,\ldots,N_{\text{int}} - 1$, as for interval a_j, let

$$\delta_{k+1} = \delta_{k+1}^* + \sum_{k=m_j}^{a_j-1} L_{j,k}^*(\eta_{j,k}^s - \eta_{j,k}^u)\left(x_j^k + x_j^{k+1}\right) + L_{j,a_j}^*\left(x_j^{a_j} - x_j^t\right) - (L_j - L_{j,a_j}^*)\left(x_j^t - x_j^{a_j+1}\right) - \sum_{n=a_j+1}^{k} (L_j - L_{j,n}^*)(\eta_{j,n}^s - \eta_{j,n}^u)\left(x_j^n - x_j^{n+1}\right)$$

Substitute Eq. A9

$$\delta_{k+1}=\delta_{k+1}^*+L_j\left(x_j^t-x_j^s\right)-\sum_{n=k+1}^{N_{\text{int}}} L_{j,n}^*(\eta_{j,n}^s-\eta_{j,n}^u)\left(x_j^n-x_j^{n+1}\right)-L_j\left(x_j^t-x_j^{a_j+1}\right)-\sum_{n=a_j+1}^{k} L_j(\eta_{j,n}^s-\eta_{j,n}^u)\left(x_j^n-x_j^{n+1}\right)$$

Again, since

$$L_j\left(x_j^t-x_j^s\right)\geq \sum_{n=k+1}^{N_{\text{int}}} L_{j,n}^*(\eta_{j,n}^s-\eta_{j,n}^u)\left(x_j^n-x_j^{n+1}\right)+L_j\left(x_j^t-x_j^{a_j+1}\right)+\sum_{n=a_j+1}^{k} L_j(\eta_{j,n}^s-\eta_{j,n}^u)\left(x_j^n-x_j^{n+1}\right),$$

$\delta_{k+1}\geq\delta_{k+1}^*$, for $k=a_j+1,\dots,N_{\text{int}}-1$.

For the last interval N_{int}, it must hold that $\delta_{N_{\text{int}}+1}=\delta_{N_{\text{int}}+1}^*=0$. Indeed, following the manipulations above, we have

$$\delta_{N_{\text{int}}+1}=\delta_{N_{\text{int}}+1}^*+\sum_{k=m_j}^{a_j-1} L_{j,k}^*(\eta_{j,k}^s-\eta_{j,k}^u)\left(x_j^k-x_j^{k+1}\right)+L_{j,a_j}^*\left(x_j^{a_j}-x_j^t\right)-(L_j-L_{j,a_j}^*)\left(x_j^t-x_j^{a_j+1}\right)-\sum_{n=a_j+1}^{N_{\text{int}}}(L_j-L_{j,n}^*)(\eta_{j,n}^s-\eta_{j,n}^u)\left(x_j^n-x_j^{n+1}\right)$$

Substitute Eq. A9 and Eq. A8

$$\delta_{k+1}=\delta_{k+1}^*+L_j\left(x_j^t-x_j^s\right)-L_j\left(x_j^t-x_j^{a_j+1}\right)-\sum_{n=a_j+1}^{N_{\text{int}}} L_j(\eta_{j,n}^s-\eta_{j,n}^u)\left(x_j^n-x_j^{n+1}\right)$$

$$=\delta_{k+1}^*+L_j\left(x_j^t-x_j^s\right)-L_j\left(x_j^t-x_j^s\right).$$

Therefore, it holds that $\delta_{N_{\text{int}}+1}=\delta_{N_{\text{int}}+1}^*=0$.

Thus, a new set of $\delta_k\geq\delta_i^*$, $k=1,\dots,N_{\text{int}}+1$, has been obtained.

The entire procedure needs to be repeated for every other lean stream that has some of the nonzero optimal flow rates of its associated set of lean substreams different from one another. To simplify the notation, reassign $\delta_k^*\leftarrow\delta_k$. Define variables as above for the next such set of lean substreams and so on until a new $L_j=L_{j,N_{\text{int}}}^*$ and x_j^t have been defined for every lean stream that satisfies this criterion. For the remaining lean streams, define ($L_j=L_{j,N_{\text{int}}}^*$, $x_j^t=x_j^{m_j}$, $j=1,\dots,N_S$), where m_j is the interval index of the top-most substream whose optimal flow rate is nonzero ($L_{j,k}^*=0$, $k=1,\dots,m_j-1$, and $L_{j,k}^*=L_{j,k+1}^*>0$, $k=m_j,\dots,N_{\text{int}}$). This change will not alter the δ_k or δ_k^*, since identical component balances around the same intervals are involved.

Next, if any rich stream has associated with it some substreams whose nonzero optimal flow rates are different, then replace the set of $R_{i,k}$, $k=1,\dots,N_{\text{int}}$ substreams by a stream with inlet composition y_i^s, a flow rate G_i, and a target composition y_i^t defined as

$$y_i^t=y_i^s-\sum_{k=1}^{m_i}\frac{G_{i,k}^*}{G_{i,1}}(\lambda_{i,k}^l-\lambda_{i,k}^s)(y_i^k-y_i^{k+1}),\qquad\text{(A10)}$$

where the summation term in the righthand side of the above definition is the cumulative load of substreams associated with the ith stream, and m_i is the interval such that the exit composition of the bottom-most $R_{i,k}$ for which $G_{i,k}^*>0$ is $y_i^{m_i+1}$.

Following logic similar to that for the lean substreams, it can be shown that $\delta_k\geq\delta_k^*$, $k=1,\dots,N_{\text{int}}+1$. Thus, a new set of $\delta_k\geq\delta_k^*$, $\forall k\in K$ can be obtained. The process needs to be repeated for every other rich stream that satisfies the above criteria. To simplify the notation, reassign $\delta_k^*\leftarrow\delta_k$. Define a replacement stream, as above, for the next such set of rich substreams, until a new $G_i=G_{i,1}$, and y_i^t have been defined as above for every rich stream following this criteria. For the remaining rich streams, define ($G_i=G_{i,1}$, $y_i^t=y_i^{m_i}$, $i=1,\dots,N_S$), where m_i is the interval index of the bottom-most substream whose optimal flow rate is nonzero ($G_{i,k}^*=G_{i,1}$, $k=1,\dots,m_i-1$, and $G_{i,k}^*=0$, $k=m_i,\dots,N_{\text{int}}$). This change will not alter the δ_k or δ_k^*, since identical component balances around the same intervals are involved. Moreover, since $L_i=L_{j,N_{\text{int}}}^*$, $j=1,\dots,N_S$, then $\mu=\nu^*$. Thus, a feasible point to problem 10 has been obtained from the optimal solution of problem 23, with identical objective value. Therefore, in this case as well, $\nu^*\geq\mu^*$.

Thus, a feasible point has been obtained for problem 10 from $\boldsymbol{w}^*$, with

- $L_j=L_{j,N_{\text{int}}}^*$ for $j=1,\dots,N_S$;
- lean stream target compositions x_j^t defined as in Eq. A4, for $j=1,\dots,N_S$;
- $G_i=G_{i,1}$ for $i=1,\dots,N_R$;
- rich stream target compositions y_i^t defined as in Eq. A10, for $i=1,\dots,N_S$;
- δ_k for $k=1,\dots,N_{\text{int}}+1$ defined as above; and
- $\mu=\nu^*$.

Since for both cases, it is established that $\mu=\nu^*$, it then holds that $\nu^*\geq\mu^*$ Q.E.Δ. ■

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