# Synthesis of Mass Exchange Networks

The purpose of this work is to introduce the notion of synthesizing mass-exchange networks (MEN's). A systematic, two-stage, procedure is proposed for the synthesis of cost-effective MEN's. In the first stage, a thermodynamically-oriented procedure is used to identify the thermodynamic bottlenecks (pinch points) that limit the extent of mass exchange between the rich and the lean process streams. Preliminary networks, that feature maximum mass exchange, are generated at this stage. The objective of the second stage is to improve the design of these preliminary networks so as to develop a final configuration of the MEN that satisfies the assigned exchange duty at minimum venture cost. This approach is applied to the synthesis of MEN's with single-component targets as well as multicomponent, compatible targets. An illustrative example on the sweetening of coke-oven gas is presented to demonstrate the applicability of the proposed synthesis procedure.

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## Introduction

The area of chemical process synthesis has received considerable attention over the past two decades. Extensive reviews on the large number of publications in this field can be found in the literature (e.g., Hendry et al., 1973; Hlavacek, 1978; Nishida et al., 1981). In particular, the problem of separation-system synthesis has been the subject of vigorous research effort due to the significant capital and operating costs associated with the separation processes used in chemical plants. The task of separation-system synthesis can be defined as follows (e.g., Floudas, 1987): "Given a set of multicomponent feed streams of known conditions, synthesize a separation sequence that can separate the feed streams into several multicomponent product streams of known conditions with a minimum venture cost." One way of classifying separation processes is according to the nature of the separating agent used which may take the form of energy or mass (King, 1980). Examples of energy-separating-agent processes are distillation, crystallization, and evaporation, while common mass-separating-agent processes are absorption, desorption, ion-exhcnage, etc. Research efforts in the field of separation-system synthesis have primarily been concerned with the synthesis of distillation-based separation systems. A very good reivew of the synthesis approaches for distillation trains is provided by Westerberg (1985). Surprisingly, much less attention has been directed toward the other important category of separators, namely those using mass-separating agents (MSA's) such as solvents, adsorbents, etc.

The earliest attempts to synthesize separation systems which involve the use of MSA's date back to the early 70's. Rudd and coworkers (Siirola et al., 1971; Rudd et al., 1973) developed a heuristic approach for the synthesis of multicomponent separation sequences, as a part of a general process-flowsheeting program called AIDES. Thompson and King (1972) used heuristic and algorithmic programming to select both the sequence and types of separation processes. Stephanopoulos and Westerberg (1976) proposed an evolutionary approach to the synthesis of multicomponent separation sequences. Later, this strategy was refined by Seader and Westerberg (1977), who developed a combined heuristic and evolutionary strategy for the synthesis of simple separation sequences. Motard and coworkers (Mahalec and Motard, 1977; Nath and Motard, 1981; Lu and Motard, 1985) developed a computer methodology for synthesizing preliminary flowsheets, in which separation tasks are synthesized and cost estimated using a set of heuristic and evolutionary rules. Liu and his colleagues (Nadgir and Liu, 1983; Liu 1987; Cheng and Liu, 1988) proposed a simple-ordered heuristic technique for the preliminary synthesis of sloppy multicomponent separation sequences. They developed flexible and effective tools to represent the synthesis problem and to analyze the technical feasibility of separation tasks or product splits. A mixed (real-integer) programming approach for the synthesis of integrated process flowsheets has been proposed by Grossmann (1985). This formulation can serve as a framework for the synthesis of separation systems. Douglas (1985) presented a hierarchical decision procedure for process synthesis which provides useful qualitative criteria for the separation-task selection. Floudas (1987) parametrized the problem using a superstructure, which embeds alternative separation configurations of interest. The solution of a nonlinear programming problem then determines the final network configuration. Muraki and Hayakawa (1988) developed a two-stage evolutionary strategy for the synthesis of multicomponent separation processes with nonsharp separators. The first stage is to identify the separation sequence, while the second is to search for the degrees of separation.

Despite the considerable contributions accomplished by the aforementioned synthesis methods, all these procedures have a common limitation: they have not addressed the problem of minimizing the cost of MSA's subject to the thermodynamic constraints imposed by the phase-equilibrium relations. By overlooking the economics of the required MSA's or the thermodynamics of the mass-transfer operations, the resulting procedures may generate separation systems which are economically unfavorable or thermodynamically infeasible. In addition, if the existing plant resources are not included *a priori* in the synthesis procedure, the generated network may preclude their use as process MSA's because of the inability of these procedures to assess thermodynamic infeasibilities. These serious limitations can be mitigated by introducing the notion of mass-exchange network (MEN) synthesis.

By "MEN synthesis," we mean the systematic generation of a cost-effective network of mass exchangers with the purpose of preferentially transferring certain species from a set of rich streams to a set of lean streams. A mass exchanger can be virtually any countercurrent, direct-contact mass-transfer operation that uses an MSA (e.g., absorption, desorption, adsorption, liquid-liquid extraction, leaching, and ion exchange). Potential candidates for the use of MEN's in chemical process industries abound in the situations of feed preparation, product separation, product finishing, and recovery of valuable materials. The recent strong emphasis on waste minimization provides an additional dimension to the industrial application of MEN synthesis. The problem of designing a recycle/reuse network for hazardous-waste minimization is often characterized by the existence of a considerable number of process streams which may be rich or lean in some species. The task of preferentially transferring a set of hazardous species from the rich streams to the lean streams can be solved effectively through a MEN-synthesis approach.

The analogy between the transfer of mass and heat has long been recognized; thus, in many respects, the mass transfer from a set of rich streams to a set of lean streams corresponds to the heat transfer from a set of hot streams to a set of cold streams. It should be pointed out, however, that a straightforward extension of the HEN technology to the synthesis of MEN's is not possible. This is attributed to the fundamental differences between the mechanism of transport and the equilibrium criteria in both cases. Indeed, the synthesis of MEN's represents a more general and a higher dimensional problem than that of HEN's. In heat exchange, thermal equilibrium simply implies that the temperature of both the hot stream and the cold stream is the same regardless of the identity of each stream. Thus, in the synthesis of HEN's, temperature represents the sole equilibrium criteria for the system irrespective of the number or the nature of the streams. On the other hand, it is the phase equilibrium characteristics of the solute-solvent system that govern the solute distribution between two phases in mass exchange. Another significant difference between HEN and MEN synthesis stems from the number of transferrable, conserved quantities in the latter case. Indeed, in HEN synthesis only energy is transferred, whereas in MEN synthesis transfer of several conserved species occurs.

The objective of the present work is to present a systematic procedure for the synthesis of MEN's. This procedure establishes two design targets prior to designing the network: the minimum cost of external MSA's and the minimum attainable number of units. Using thermodynamic considerations, the procedure first generates networks featuring the minimum cost of external MSA's. Next, these designs are improved by trading off capital cost against operating cost to minimize the total venture cost.

It should be emphasized that the present work is not intended to solve the MEN synthesis problem in its general form. Rather, it poses the problem and identifies a class of practical MEN problems, for which useful insights can be gained from the major concepts developed for the synthesis of HEN's, especially the significant contributions of Hohmann (1971), and Linnhoff and his coworkers (Linnhoff and Hindmarsh, 1983; Linnhoff and Flower, 1978). The applicability of the proposed synthesis procedure is demonstrated through an illustrative example on the design of a MEN for the sweetening of coke-oven gas.

## Problem Description

### *Problem statement*

The general MEN synthesis problem can be stated as follows:
Given a set $R = \{i | i = 1, N_R\}$ of rich process streams, a set $S = \{j | j = 1, N_S\}$ of lean process streams (or process MSA's) and a set $E = \{j | j = N_S + 1, N_S + N_E\}$ of auxiliary lean external streams (or external MSA's), synthesize a network of mass exchanger units that can preferentially transfer a set $P = \{p | p = 1, N_P\}$ of certain species from the rich streams to the lean streams at minimum venture cost.

Each rich stream has a mass flow rate $G_i$ and has to be brought from a supply composition $Y_i^s = \{y_{p,i}^s | p \in P\}$ to a target composition $Y_i^t = \{y_{p,i}^t | p \in P\}$. Similarly, each lean process stream has a supply composition $X_j^s = \{x_{p,j}^s | p \in P\}$ and a target composition $X_j^t = \{x_{p,j}^t | p \in P\}$ which should not exceed a certain constrained value $x_{p,j}^c$, i.e.

$$x_{p,j}^t \leq x_{p,j}^c \quad \forall\, p \in P \tag{1a}$$

The nature of such a constraint may be:

- Physical, e.g., maximum solubility of solute in solvent
- Economic to optimize the cost of any subsequent separation of the effluent lean stream
- Technical to avoid excessive corrosion, viscosity, or fouling
- Envrionmental as imposed by some environmental protection regulation

The flow rate of each lean process stream is bounded by the following availability constraint

$$L_j \leq L_j^c \tag{1b}$$

Each auxiliary lean external stream has a supply composition $X_j^s$; again, its target composition is constrained as expressed by Eq. 1a. The mass flow rate of any external MSA is flexible and should be determined according to the economic considerations of the network synthesis.

To outline the essence of our design methodology, we have chosen to employ several assumptions which simplify the exposition of our procedure. Nonetheless, it should be emphasized that these assumptions simply streamline the presentation of our ideas and can be relaxed at the expense of a more cumbersome formalism.

### *Basic assumptions*

Without loss of generality, the proposed synthesis procecure utilizes the following assumptions:

1. The mass flow rate of each stream remains essentially unchanged as it passes through the network.
2. Within the MEN, stream recycling is not allowed.
3. In the range of compositions involved, any equilibrium relation governing the distribution of a transferrable component, $p$, between the $i$th rich stream and the $j$th lean stream is linear and independent of the presence of other soluble components in the rich stream,

$$y_p = m_{p,j}x_{p,j} + b_{p,j} \quad j = 1, 2, \ldots, N_S + N_E \text{ and } p \in P \quad (2)$$

where both $m_{p,j}$ and $b_{p,j}$ are assumed to be constants whose values depend on the characteristics of the binary system involving the solute $p$ and the lean stream $j$.

The first assumption is reasonable, when relatively small variations in compositions are required or when some counterdiffusion takes place from the lean streams to the rich streams. Even if the changes in flow rates are considerable, however, one can use mass flow rates of the nontransferrable (inert) components instead of those of whole streams and mass ratios (kg transferrable component/kg inert components) instead of mass fractions. The second assumption excludes the possibility of recycling and can be relaxed by formulating MEN synthesis as a mathematical programming problem. In this case, a parametric realization of the network structure is employed that can account for stream recycling within the network. The third assumption indicates that the equilibrium relations are linear over the range of operating compositions. If an equilibrium relation is nonlinear and cannot be linearized with a reasonable degree of accuracy over the operating range, one can simply linearize it over small composition ranges with the coefficients $m_{p,j}$ and $b_{p,j}$ being varied from one range to the other. The third assumption also indicates that the equilibrium relations for the transfer of the various components from the rich streams to the lean streams are mutually independent. For instance, in multicomponent gas absorption, this assumption will be valid if all, but one, of the gas components are substantially insoluble in the liquid or if ideal solutions are formed in the liquid phase. Several important industrial applications fall in these two categories.

## Problem Classification

The multicomponent nature of the MEN synthesis problem suggests that the problem be decomposed into two categories. In the first category, separation targets are set for a single (key) component. The selection of single-component separation targets is common practice in many industrial processes (e.g., $H_2S$ in sweetening of coke-oven gas, $SO_2$ in flue gas desulfurization, $CO_2$ in hydrogen/ammonia manufacture, $H_2O$ in gas drying by adsorption, $CuSO_4$ in copper leaching from calcined ores, and acetic acid extraction from aqueous acetic acid streams), even if more than one component needs to be transferred. In some separation processes, however, separation targets are set for more than one component. The class of problems that involve multiple-component separation targets constitutes the second category. Having classified the synthesis problem into two categories, we now focus on the solution of the first category.

## Design Procedure

### *Design targets*

The proposed design methodology reduces the size of this inherently combinatorial synthesis problem by establishing design targets. This is achieved without prior commitment to any particular network configuration. Indeed, the rationale behind the development of these targets is based on the thermodynamic and combinatorial properties of the posed problem.

*Minimun cost of MSA's.* Thermodynamics determines the minimum cost of the MSA's to be used. When using a single external MSA, the objective will be to minimize the amount of this lean stream. This target aims at minimizing the operating cost of the network. In many industrial applications, this target has a profound impact on the economics of the separation system. For example, in gas absorption, Astarita et al. (1983, p.26) stated that: "Solvent circulation rate is the single most important factor in the economics of gas treating with chemical solvents. Solvent circulation rate, through its influence on the size of pumps, lines, heat exchangers, and regeneration tower, has a large influence on the capital cost of gas treating plants. Solvent rate also has a major influence on the energy (steam) requirement for solvent regeneration, because the reboiler heat duty is associated directly with liquid rate." Any network featuring the minimum cost of MSA's will be referred to as a *minimum-utility network*.

*Minimum Number of Mass Exchanger Units.* Combinatorics determines the minimum number of mass exchanger units that is required in the network. This objective attempts to minimize indirectly the fixed cost of the network since the cost of each mass exchanger is usually a concave function of the unit size. Furthermore, in a practical context it is desirable to minimize the number of separators, since this will generally correspond to less pipework, foundations, maintenance, and instrumentation. Normally, the minimum number of units is related to the total number of streams by the following expression (Linnhoff et al., 1979):

$$U = N_R + N_S + N_E - N_i \quad (3)$$

where $N_i$ is the number of independent synthesis subproblems into which the original synthesis problem can be subdivided.

This procedure can identify the existence of thermodynamic bottlenecks that may lead to a mutual incompatibility between the two aforementioned design targets. In such cases, the procedure can generate several networks that trade off capital costs against cost of external MSA's.

Throughout this paper, we shall illustrate the basic concept of the proposed synthesis procedure by considering the following example on the sweetening of coke-oven gas (COG). The technical data involved in this example are adapted from the literature (Kohl and Reisenfeld, 1985; Astarita et al., 1983; Maadah and Maddox, 1978; Massey and Dunlap, 1975).

## Example Problem: Sweetening of COG

The basic objective of COG sweetening is the removal of acidic impurities, primarily hydrogen sulfide, from COG (a mixture of $H_2$, $CH_4$, CO, $N_2$, $NH_3$, $CO_2$, and $H_2S$). Hydrogen

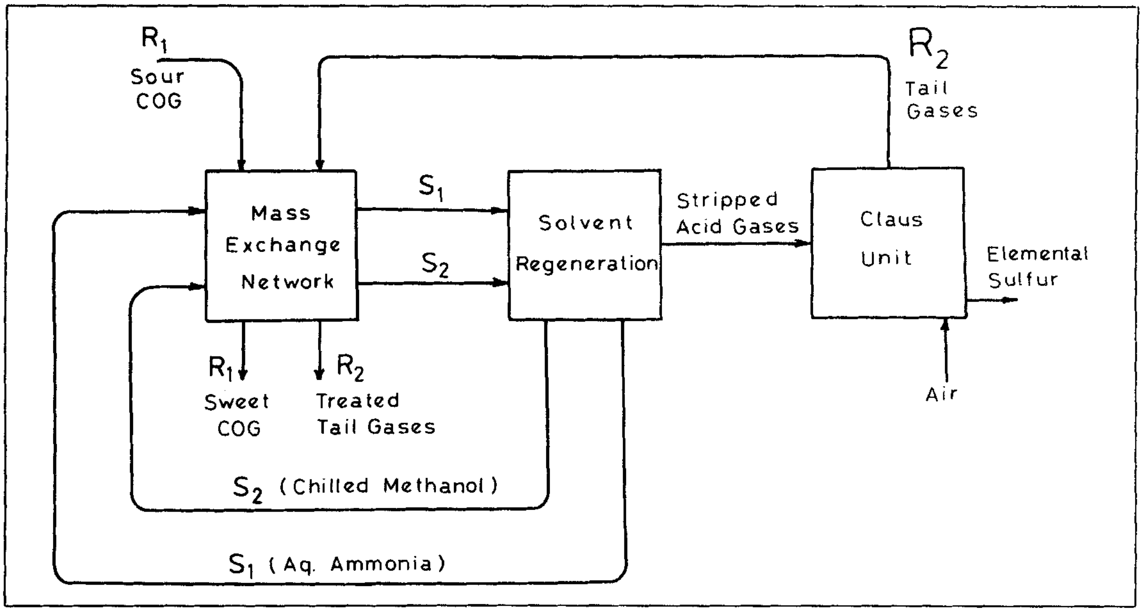


**Figure 1. A recycle/reuse unit for COG sweetening.**

sulfide is an undesirable impurity, because it is corrosive and contributes to $SO_2$ emission when the COG is used as a fuel. The natural presence of ammonia in COG led to the utilization of aqueous ammonia as a solvent (process lean stream, $S_1$). It is desirable that the ammonia recovered from the sour gas compensates exactly the ammonia losses throughout the system and, thus, eliminates the need for ammonia makeup. Besides ammonia, an external MSA (chilled methanol, $S_2$) is also available for service to supplement the aqueous ammonia solution as needed. The purification of the COG involves washing the sour COG, $R_1$, with sufficient aqueous ammonia and/or chilled methanol to absorb the required amounts of hydrogen sulfide. The acid gases are subsequently stripped from the solvents and the regenerated MSA's are recirculated. The stripped acid gases are fed to a "Claus unit" where elemental sulfur is recovered from hydrogen sulfide. In view of air pollution control regulations, the tail gases leaving the Claus unit, $R_2$, ought to be treated for partial removal of the unconverted hydrogen sulfide. According to the current industrial practice, "Claus off-gas treating processes are scaled-down replicas of the mainstream acid gas separation unit" (Astarita et al., 1983, p. 247). The design and construction of two separate networks for the treatment of the mainstream of COG and the Claus off-gas offers no obvious economic advantages and therefore we propose a more general configuration in which the tail gases are recycled to a MEN whereby the residual hydrogen sulfide is partially removed. Prior to feeding the tail gases to the MEN, a small portion of this stream is purged to prevent accumulation of impurities. The basic features of the proposed process are illustrated in Figure 1.

In the range of compositions involved, the equilibrium solubility data for hydrogen sulfide in aqueous ammonia and methanol may be correlated by the following relations, respectively:

$$y_1 = 1.45x_{1,1}$$

and

$$y_1 = 0.26x_{1,2}$$

where the first subscripts, $p = 1$, correspond to hydrogen sulfide, and the second subscripts, $j = 1, 2$, correspond to aqueous ammonia and methanol, respectively. Table 1 summarizes the data for all the streams. The design task at hand is to synthesize a cost-effective MEN that can handle the assigned separation duties.

### Composition interval table

The notion of a composition interval table (CIT) can be utilized to incorporate thermodynamic constraints into the synthesis procedure. The CIT employs several composition scales that are in a one-to-one correspondence with one another. To establish this correspondence among several composition scales, we first introduce the notion of "minimum allowable composition difference."

Consider the mass exchanger shown in Figure 2. A material balance on a solute $p$ that is transferred from stream $i$ to stream $j$, is given by

$$G_i(y_{p,i}^{in} - y_{p,i}^{out}) = L_j(x_{p,j}^{out} - x_{p,j}^{in}) \tag{4}$$

which represents the operating-line equation. On the other hand, the equilibrium-line relation is given by Eq. 2. Suppose that it is required to reduce the composition of the rich stream from $y_{p,i}^{in}$ to $y_{p,i}^{out}$ and that the ratio $L_j/G_i$ is not fixed. When the value of $x_{p,i}^{in}$ is specified, the maximum theoretical outlet composition of the lean stream, $x_{p,j}^{out,*}$, is in equilibrium with $y_{p,i}^{in}$. An infi-

**Table 1. Data for the Streams of Example Problem for Hydrogen Sulfide**

| Rich Streams | | | | Lean Streams | | | |
|---|---|---|---|---|---|---|---|
| Stream | $G_i$ kg/s | $y_{1,i}^s$ | $y_{1,i}^t$ | Stream | $L_j^c$ kg/s | $x_{1,j}^s$ | $x_{1,j}^t$ |
| $R_1$ | 0.9 | 0.0700 | 0.0003 | $S_1$ | 2.3 | 0.0006 | 0.0310 |
| $R_2$ | 0.1 | 0.0510 | 0.0001 | $S_2$ | ∞ | 0.0002 | 0.0035 |

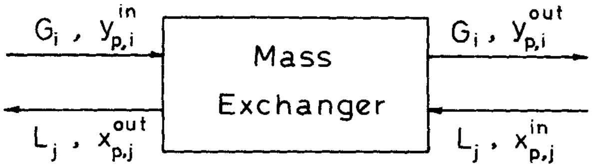


**Figure 2. A mass exchanger.**

nitely large exchanger, however, is needed to undertake this transfer duty. Therefore, it is necessary to assign a minimum value for the difference between the operating and the equilibrium compositions of the lean stream in order to avoid designing an excessively large unit. This value is called the minimum allowable composition difference and is denoted by $\epsilon_{p,j}$ (Figure 3a).

Similarly, when $x_{p,j}^{out}$ is specified, the maximum theoretical inlet composition of the lean stream, $x_{p,j}^{in,*}$, is in equilibrium with $y_{p,i}^{out}$. However, as shown in Figure 3b, the maximum practically feasible inlet composition of the lean stream, $x_{p,j}^{in,max}$, is $x_{p,j}^{in,*}$ less $\epsilon_{p,j}$.

Therefore, for any prevailing value of $y_{p,i}$, it is practically feasible to transfer the solute $p$ from a rich stream to a lean stream when the following condition is satisfied

$$x_{p,j} \le \frac{y_{p,i} - b_{p,j}}{m_{p,j}} - \epsilon_{p,j} \qquad (5a)$$

with the equality applying in the cases where the maximum practically feasible composition of component $p$ in the lean stream is attained, i.e.

$$x_{p,j}^{max} = \frac{y_{p,i} - b_{p,j}}{m_{p,j}} - \epsilon_{p,j} \qquad (5b)$$

The minimum allowable composition difference is an optimizable parameter. When $\epsilon_{p,j}$ is close to zero, infinitely large separators will be required and, consequently, the capital cost of the network will be infinite. The cost of MSA's, however, will be at a minimum. When $\epsilon_{p,j}$ is increased, the operating cost will increase whereas the fixed cost will decrease. In general, the annualized total cost will pass through a minimum which corresponds to the optimal value of the minimum allowable composition difference. For simplicity, throughout this paper the value of $\epsilon_{p,j}$ will be fixed at 0.0001. Having established the notion of minimum allowable composition difference, we are now in a position to construct the CIT.

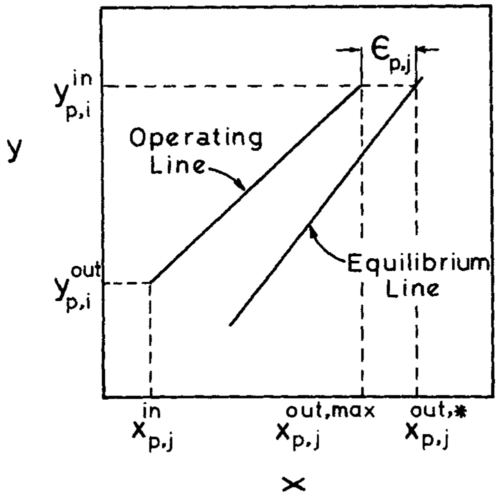


**Figure 3a. Minimum allowable composition difference at the rich end.**

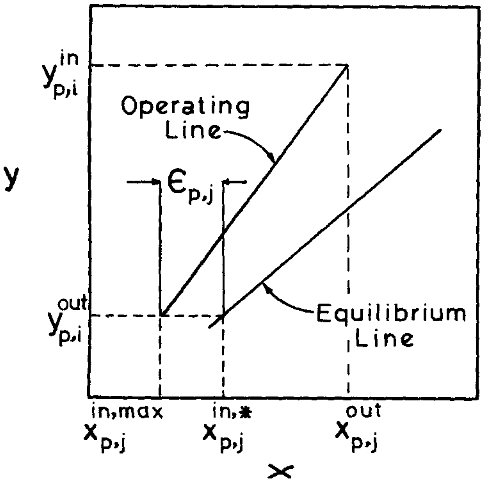


**Figure 3b. Minimum allowable composition difference at the lean end.**

In this diagram, $N_S+1$ composition scales for component $p$ are generated. First, a composition scale, $y_p$, for the rich streams is established. It is worth pointing out that, according to the third assumption, the equilibrium relations are indifferent to the presence of other soluble components in the rich streams. This allows the use of a single scale, $y_p$, for the component $p$ in all the rich streams, although each rich stream may contain several components which do not exist in the other streams. Then, using Eq. 5b, one can readily create the $N_S$ corresponding composition scales for the lean process streams.

On the CIT, any process stream is represented by an arrow. The tail of each arrow corresponds to the supply composition of that stream, while the head represents the target composition for a rich stream or the constrained outlet composition for a lean stream. Next, we establish a series of composition intervals that often correspond to the heads and tails of these arrows. In this case, the number of the problem intervals can be related to the total number of process streams through the following expression

$$N_{int} \le 2(N_R + N_S) - 1 \qquad (6)$$

with the equality applying in cases where no two heads or tails coincide.

Aside from the stream representations, the CIT includes five columns. Column 1 represents the surplus of mass of component $p$ available for transfer in each interval. For the $k$th interval, the surplus term, $\Delta_{p,k}$, corresponds to the difference between the mass of species $p$ to be transferred from the rich streams and the mass of species $p$ to be transferred to the lean process streams in this interval, i.e.

$$\Delta_{p,k} = \Sigma\, G_i(y_{p,k} - y_{p,k+1}) + \Sigma\, L_j(x_{p,j,k+1} - x_{p,j,k}) \qquad (7)$$

where the summations are taken over the process streams present in the $k$th interval only. For any given interval, if the mass of species $p$ available in the rich streams is greater than that transferrable to the lean process streams, then the parameter $\Delta_{p,k}$ is positive; otherwise, it is negative.

In each subnetwork, the component $p$ can be transferred from the rich streams to the lean streams, because the thermodynamic constraints are guaranteed to be satisfied. Of course, it is also feasible to transfer component $p$ from any rich stream at a given composition interval to any lean stream at lower composition intervals. In other words, positive mass surplus can be passed on from higher to lower composition intervals.

Columns 2 and 3 of the CIT represent the cumulative flows of mass of species $p$ available for transfer. It is initially assumed that each lean process stream leaves the network at its specified constrained outlet composition. This is represented by a zero input to the first interval (Column 2). Based on this initial assumption, one can readily calculate the output from the first interval by simply adding the surplus to the input. This output is passed on to the next interval and, therefore, forms the input to the second interval. The same procedure is then repeated for all composition intervals.

It should be noted that it is not feasible to transfer negative output mass flow from one interval to the next. Therefore, if Columns 2 and 3 of the CIT contain any negative figures, the input to the first interval must be increased, and both Columns 2 and 3 must be modified. Such a modification appears in Columns 4 and 5. In Column 4, the input to the first interval ought to be large enough to guarantee the nonnegativity of all the figures appearing in Columns 4 and 5. The minimum increase in the input to the first interval is equal to the absolute value of the most negative number appearing in Column 2 or 3. Having identified the modified input to the first interval, one can easily calculate all the elements of Columns 4 and 5 using exactly the same sequence of calculations as Columns 2 and 3. The CIT for the example problem is illustrated in Table 2.

Based on the rationale followed in constructing the CIT, the following two values in Columns 4 and 5 have important physical significance:

1. The top figure in Column 4 (0.00283 kg/s) represents the excess capacity of the aqueous ammonia to remove $H_2S$. Owing to thermodynamic considerations, this excess cannot be used in removing the solute $p$ from the rich streams. According to the designer's preferences or to the specific requirements of the process, such as excess can be eliminated from service by reducing the outlet composition and/or the mass flow rate of one or more of the lean process streams. If, for instance, it is desirable to reduce the flow rate of aqueous ammonia, then

$$L_1 = 2.3000 - 0.00283/(0.0310 - 0.0006)$$
$$= 2.2069 \text{ kg/s}.$$

2. The bottom figure in Column 5 (0.00074) denotes the minimum mass of $H_2S$ to be removed by the external MSA. Therefore, the minimum flow rate of chilled methanol required to supplement the separation duty is given by

$$L_2 = 0.00074/(0.0035 - 0.0002)$$
$$= 0.2242 \text{ kg/s}.$$

### *Pinch concept*

Another important feature of the CIT is the possible existence of a point at which the cumulative flow of mass available for transfer vanishes. This point is called the "pinch point." In Table 2, the pinch point lies between the third and the fourth intervals. The pinch point is regarded as a thermodynamic bottleneck that precludes any further integrated mass exchange between the rich and the lean process streams. In other words, the pinch represents the most constrained region of a design, since all matches between the rich and the lean streams at the pinch point are subject to the minimum allowable composition difference.

Figure 4 demonstrates another way of locating the pinch for a component $p$. Consider that two rich and two lean process streams are available. Then, using Eq. 5b, one can establish the correspondence between the three composition scales $y_p$, $x_{p,1}$, and $x_{p,2}$. Next, the mass of component $p$ exchanged by each stream is plotted against its composition scale according to the following equations:

Mass transferred from the $i$th rich stream

$$G_i(y_{p,i}^{\text{in}} - y_{p,i}^{\text{out}})$$

where

$$i = 1, 2, \dots, N_R \tag{8}$$

**Table 2. Composition Interval for Hydrogen Sulfide**

| | | | | | | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|---|---|---|---|---|
| | Rich Streams | | | Lean Streams | | | Cumulative Mass Available | | Modified Cumulative Mass Available | |
| Interval | $y_1$ 0.0700 | $R_1$ | | $x_{1,1}$ 0.0482 | | Surplus kg/s | Input kg/s | Output kg/s | Input kg/s | Output kg/s |
| 1 | | | $R_2$ | | | 0.01710 | 0.0000 | 0.01710 | 0.00283 | 0.01994 |
| | 0.0510 | | | 0.0351 | | | | | | |
| 2 | | | | | | 0.00590 | 0.01710 | 0.02300 | 0.01994 | 0.02584 |
| | 0.0451 | | | 0.0310 | | | | | | |
| 3 | | | | | | −0.02584 | 0.02300 | −0.00283 | 0.02584 | 0.00000 |
| | 0.0010 | | | 0.0006 | | | | | | |
| 4 | | | | | $S_1$ | 0.00072 | −0.00283 | −0.00212 | 0.00000 | 0.00072 |
| | 0.0003 | | | 0.0001 | | | | | | |
| 5 | | | | | | 0.00002 | −0.00212 | −0.00210 | 0.00072 | 0.00074 |
| | 0.0001 | | | 0.0000 | | | | | | |

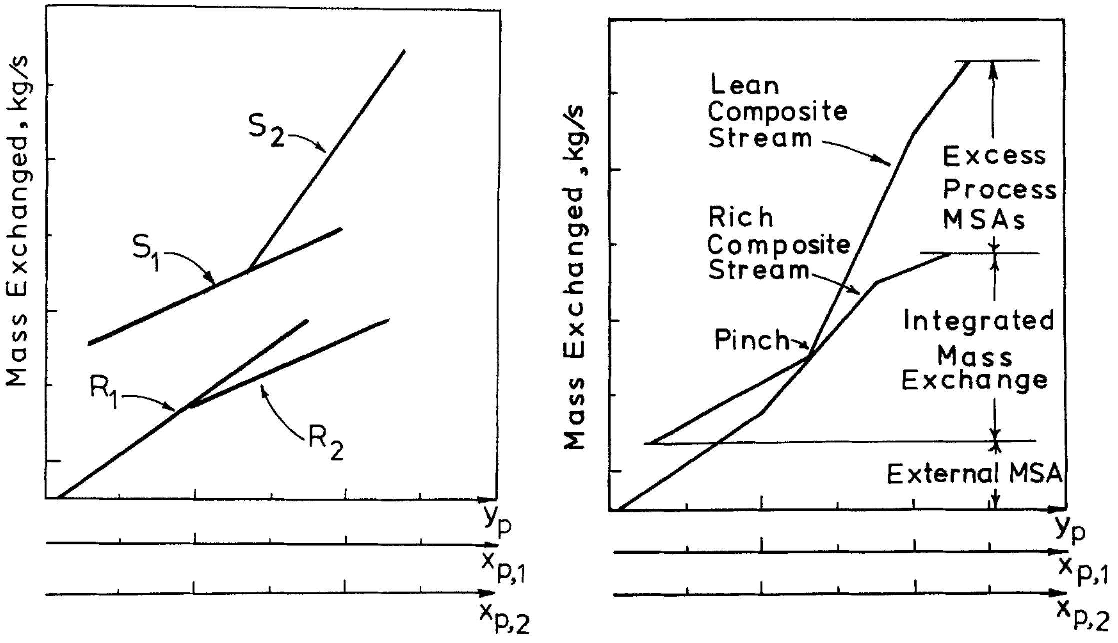


**Figure 4. Graphical location of the pinch.**

and mass transferred to the $j$th lean stream:

$$L_j(x^{out}_{p,j} - x^{in}_{p,j})$$

where

$$j = 1, 2, \ldots, N_S \qquad (9)$$

In Figure 4a, the vertical scale is only relative; therefore, any stream can be moved upward or downward on this diagram.

Figure 4b shows a plot of cumulative exchanged mass of component $p$ vs. composition. The cumulative curves for the rich process streams and for the lean process streams are called the "composite rich stream" and the "composite lean stream," respectively. On this diagram, thermodynamic feasibility of mass exchange is ensured, when the lean composite stream is always above the rich composite stream. Therefore, the lean composite stream can be slid down until it touches the rich composite stream. The point where the two curves touch is the pinch point. The overlap between the composite curves represents the maximum feasible amount of mass exchange among the rich and the lean process streams. Having identified the pinch point, one can easily evaluate the excess mass of species $p$ available for transfer in the lean process streams as well as the minimum mass of component $p$ to be removed by the external MSA's, Figure 4b. Thus, this diagram generates exactly the same information that can be obtained from the CIT.

As can be seen from Figure 4b, the pinch decomposes the synthesis problem into two regions: a rich end and a lean end. The rich end comprises all streams or parts of streams richer than the pinch composition. Similarly, the lean end includes all the streams or parts of streams leaner than the pinch composition. Above the pinch, exchange between only the rich and the lean process streams takes place. External MSA's are not required. Using an external MSA above the pinch will incur the penalty of eliminating an equivalent amount of the process lean streams from service. On the other hand, below the pinch, both the process and the external lean streams should be used.

Furthermore, Figure 4b indicates that, if any mass is transferred across the pinch, the composite lean stream will move upward and, consequently, external MSA's in excess of the minimum requirement will be used. Therefore, for the minimum cost of external MSA's, it is not permitted to transfer mass across the pinch.

Regardless of the adopted synthesis procedure, the minimum cost of external MSA's will never be attained if the procedure creates, at an early stage, a situation which later results in transferring mass across the pinch. Thus, by starting the synthesis at the pinch, the designer can guarantee the generation of minimum-utility networks. Moreover, since the pinch represents the most constrained region of design, the number of feasible matches in this region is severely limited. Thus, when the synthesis is started at the pinch, the freedom of design choices at later steps will not be prejudiced.

The above discussion clearly shows that the synthesis of a MEN should start at the pinch and proceed in two directions separately: the rich and the lean directions. To facilitate the design procedure both above and below the pinch, we establish next feasibility criteria for the characterization of stream matches at the pinch.

## Feasibility Criteria at the Pinch

In this section, we shall discuss the feasibility criteria identifying the essential matches or topology options at the pinch. Such matches will be referred to as "pinch matches" or "pinch exchangers." The feasibility matches will also inform the designer whether or not stream splitting is required at the pinch. Once away from the pinch, these feasibility criteria do not have to be considered, and matching the rich and the lean streams becomes a relatively simple task. In order to identify the feasible pinch topologies, the following two feasibility criteria will be applied to the stream data.

### *Stream population*

In a minimum-utility design, any mass exchanger immediately above the pinch will operate with the minimum allowable composition difference at the pinch side. Since it is required to bring all the rich streams at the pinch to their pinch composition, any rich stream leaving a pinch exchanger can only operate against a lean stream at its pinch composition. Therefore, for each pinch match, at least one lean stream (or branch) has to exist per each rich stream. In other words, for a minimum-utility design, the following inequality must apply at the rich end of the pinch

$$N_{ra} \leq N_{la} \tag{10a}$$

where $N_{ra}$ is the number of rich streams or branches immediately above the pinch, and $N_{la}$ is the number of lean streams or branches immediately above the pinch. If the above inequality does not hold for the stream data, one or more of the lean streams will have to be split.

Conversely, immediately below the pinch, each lean stream has to be brought to its pinch composition. At this composition, any lean stream can only operate against a rich stream at its pinch composition or higher. Since a minimum-utility design does not permit the transfer of mass across the pinch, each lean stream immediately below the pinch will require the existence of at least one rich stream (or branch) at the pinch composition. Therefore, immediately below the pinch, the following criteria must be satisfied:

$$N_{lb} \leq N_{rb} \tag{10b}$$

where $N_{lb}$ is the number of lean streams or branches immediately below the pinch, and $N_{rb}$ is the number of rich streams or branches immediately below the pinch. Again, splitting one or more of the rich streams may be necessary to realize the above inequality.

### *Operating line vs. equilibrium line*

The second feasibility criterion is imposed by thermodynamic considerations. As illustrated by Figure 3b, for any feasible rich-end pinch exchanger, the slope of the operating line must be larger than or equal to the slope of the equilibrium line. Hence, for each rich-end pinch match, the following inequality must hold:

$$\frac{L_j}{m_{p,j}} \geq G_i \tag{11a}$$

On the other hand, as can be seen from Figure 3a, for each lean-end pinch match, the following criterion must be fulfilled:

$$\frac{L_j}{m_{p,j}} \leq G_i \tag{11b}$$

Once again, stream splitting may be required to guarantee that inequality (Eq. 11a or 11b) is realized for each pinch match.

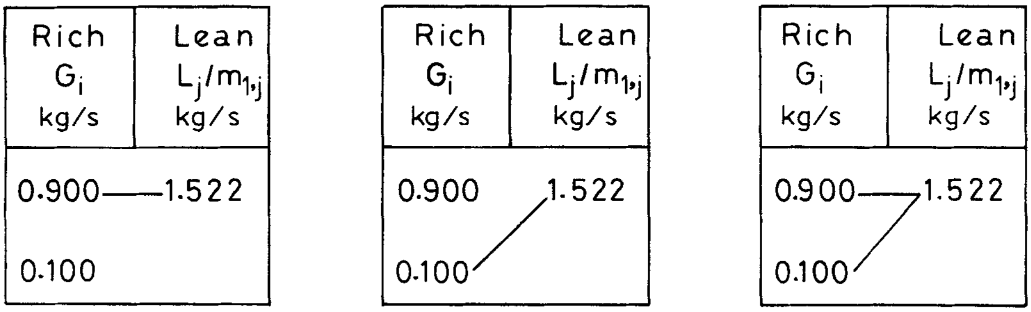
It should be emphasized again that the feasibility criteria (Eqs. 10a and 10b) ought to be fulfilled only at the pinch. Once the pinch matches are identified, it generally becomes a simple task to complete the network design. Moreover, the designer always has the freedom to violate these feasibility criteria at the expense of increasing the cost of external MSA's beyond the minimum-utility requirement.

The following representation will be used to illustrate the network structure graphically. Rich streams are represented by horizontal arrows running to the right at the top of the diagram. Compositions (expressed as weight percentages of the key component in each stream) are placed above the corresponding arrow. A match between two streams is indicated by placing a pair of circles on each of the streams and connecting them by a vertical line. Mass-transfer loads of the key component for each exchanger are noted in appropriate units (kg/s) beneath the lower circle. The exchangers are numbered in their upper circles. The pinch is represented by two vertical dotted lines.

## Example Continued

We are now in a position to demonstrate the applicability of the feasibility criteria in identifying feasible pinch topologies and generating minimum-utility networks for the example problem. Since the pinch point decomposes the problem into two subproblems—a rich end and a lean end, each subproblem will be considered as an independent synthesis task.

At the rich end of the pinch, the number of rich streams is greater than the number of lean streams and, thus, the first feasibility requirement (Eq. 10a) is not realized and $S_1$ ought to be split. The second feasibility criterion (Eq. 11a) can be easily checked through the "feasibility table" shown in Figure 5. This table serves as a simple way of comparing the values of $L_j/m_{p,j}$ with $G_i$ for each pinch match. A pinch match is represented in this table by linking the two streams with a line. Stream splits are represented by two lines emanating from the stream to be split. Application of Eq. 11a indicates that there is a feasible



a. Infeasible b. Infeasible c. Feasible

**Figure 5. Feasibility study of the rich end of example problem.**

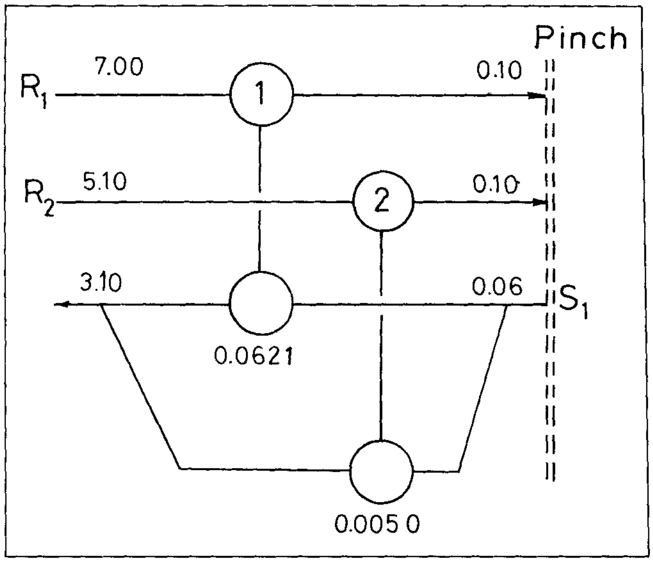


Figure 6. A rich-end design.

design option (see Figure 5c), in which stream splitting is necessary for a minimum-utility design. Figure 6 illustrates this design.

Once a match between two streams (or branches) is identified, the mass exchange load in this exchanger is taken to be equal to the smaller load of the two streams (or branches) matched. This heuristic ensures that each match will eliminate a stream (or branch) from the synthesis subproblem. Therefore, the design is steered towards the fewest possible units compatible with minimum-utility designs.

In a similar manner to the rich-end design, one can identify without difficulty two feasible matches below the pinch. Figure 7 illustrates these two lean-end matches. In Figure 7a, methanol is first exchanged with the tail gases and then with the COG. In Figure 7b, the methanol stream is split and exchanged with both rich streams.

### *Complete minimum-utility designs*

Now, it is possible to generate minimum-utility networks by combining any rich-end design with any lean-end design. For example, Figure 8 shows a minimum utility network which is obtained by combining Figures 6 with 7a. It is worth noting that minimum utility MEN's involving a large number of streams can be automatically generated without difficulty through a mathematical-programming approach (El-Halwagi and Manousiouthakis, 1988).

## Improving the Preliminary Network Designs

Based upon the basic principles of graph theory, it can be shown that a minimum-utility pinched network will generally feature more than the target minimum number of exchanger units (Linnhoff et al., 1979). Owing to the existence of a pinch which decomposes the problem into two distinct subproblems, the minimum number of units compatible with a minimum-utility design, $U_{MUD}$, is obtained by applying Eq. 3 to each subproblem separately. Therefore, for the example problem

$$U_{MUD} = (3 - 1) + (3 - 1) = 4 \text{ exchangers}$$

In other words, any minimum-utility network will involve one unit more than the target minimum number of units. Hence, a cost-effective network design ought to include a tradeoff between the number of units (capital cost) and the external MSA's (operating cost). It is, therefore, desirable to have a procedure for the systematic reduction in the number of units. This procedure involves the use of "mass-load loops" and "mass-load paths."

### *Mass-load loops*

A mass-load loop is a path connection which can be traced through a network by starting from an exchanger and returning back to the same exchanger. Generally, each extra unit will correspond to the existence of one independent loop. That is, by breaking a loop, one can eliminate one exchanger from the network. Each loop is characterized with the possibility of shifting mass-exchange loads around the loop by substracting a load from one exchanger and adding it back to another exchanger on the same stream, and so on around the loop. As a design heuristic, it is recommended to break the loop by eliminating the exchanger with the smallest mass-exchange load. Nonetheless, it has to be noted that it may not be always possible to apply this heuristic because of thermodynamic considerations. For exam-

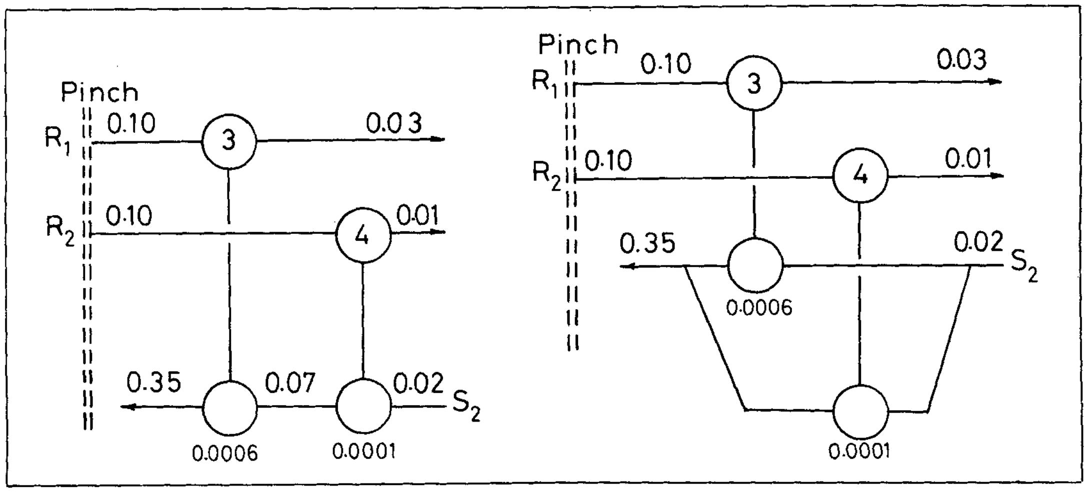


Figure 7. Two lean-end designs.

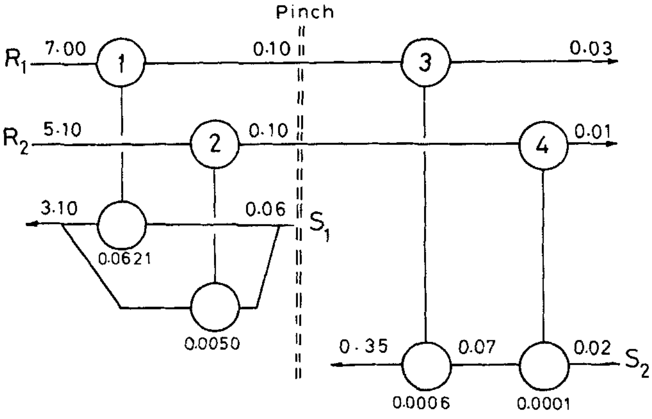


**Figure 8. A minimum-utility network for the removal of hydrogen sulfide from COG.**

ple, the network shown in Figure 8 features one unit more than the target minimum number of units. Hence, there must be one loop in the network. This loop contains the four exchangers. Any attempt to break the loop by eliminating the fourth exchanger will result in a thermodynamically infeasible situation. This infeasibility cannot be removed since the outlet composition of $R_2$ (0.01%) will have to operate with the inlet composition of $S_1$ (0.06%). Hence, in order that $R_2$ reaches 0.01%, it must be exchanged with a lean stream after leaving the second exchanger.

### *Mass-load paths*

A mass-load path is a continuous connection which starts with an external MSA and concludes with a process MSA. By shifting the loads along a path, one can add an excess amount of external MSA to replace an equivalent amount of process MSA. For instance, in Figure 8, the path $S_2$-$R_2$-$S_1$ which passes through Exchangers 4 and 2 can be used to shift a load of 0.005 kg/s from $S_1$ to $S_2$. This shift of load will lead to the elimination of the second exchanger. As imposed by Eq. 5b, the maximum practically feasible composition of $S_2$ leaving the fourth exchanger is 0.11%. Therefore, the flow rate of $S_2$ ought to be increased to become

$$L_2 = 0.0051/(0.0011 - 0.0002)$$
$$= 5.6667 \text{ kg/s}$$

In other words, when a load of 0.005 kg/s is shifted from $S_1$ to $S_2$, an exchanger is removed from the network at the expense of increasing the flow rate of $S_2$ by 5.4424 kg/s. This situation presents a tradeoff between the number of units (fixed cost) and the external MSA (operating cost). The reduced network is shown in Figure 9.

## Synthesis of MEN's with Multicomponent Targets

In this category, the separation duties are set for more than one key component. Due to the complexities associated with this category, we further classify it into the following two subproblems:

1. Synthesis of networks with compatible targets.
2. Synthesis of networks with incompatible targets.

The former subproblem is addressed in the present work, whereas the latter will be tackled in a future publication.

The problem of synthesizing a MEN with compatible targets is characterized by the property that the minimum-utility network for the "pinched" component is capable of delivering the required separation duties for all the other components. By the "pinched" component, we mean the component which requires the highest amount of external MSA for its minimum-utility design.

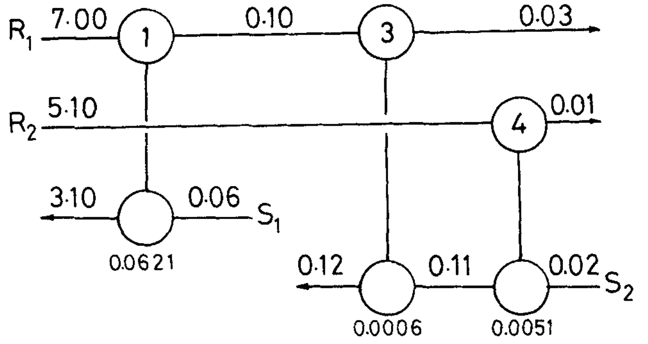


**Figure 9. A reduced network after using a mass-load path to shift a load of 0.0050 kg/s from $S_1$ to $S_2$.**

The first step in synthesizing a multicomponent compatible target MEN is to identify the pinched component by constructing the CIT for all targeted components. Then, a minimum-utility network is synthesized for the pinched component, and the mass-exchange units are therefore sized. The unit design equations are then used to calculate the compositions of all the other components throughout the network. The following example problem on COG sweetening illustrates the basic concepts of this procedure.

## COG Example

Carbon dioxide often occurs in COG in relatively large concentrations. Although it is not generally necessary to remove carbon dioxide from COG, partial removal is sometimes desirable to improve the heating value, and complete $CO_2$ elimination is required for gases undergoing processing at very low temperatures—for example, in COG purification to provide hydrogen for ammonia synthesis. In this example, we consider the case where the supply concentration of $CO_2$ in COG is 6.0 wt./wt. % and its desirable target composition is 0.5 wt./wt. %.

Carbon dioxide also represents a major impurity in the Claus tail gases. For environmental protection purposes, it is desired to reduce the content of carbon dioxide in the Claus off-gas from 11.5 to 1.0 wt./wt. %.

Over the range of operating conditions of interest, the equilibrium solubility data for carbon dioxide in aqueous ammonia and methanol may be expressed, respectively, as

$$y_2 = 0.35x_{2,1}$$

and

$$y_2 = 0.58x_{2,2}$$

where the subscript $p = 2$ refers to carbon dioxide, and the subscripts $j = 1, 2$ denote aqueous ammonia and methanol, respectively.

It is desired to synthesize a MEN that can perform the required simultaneous removal of both hydrogen sulfide and carbon dioxide in a cost-effective manner.

## Design Procedure

In the previous portion of this example, we have shown that the separation of hydrogen sulfide requires 2.2069 kg/s of aqueous ammonia as well as 0.2242 kg/s of methanol. When these flow rates are used to construct the CIT for carbon dioxide, it can be readily seen that these flow rates are larger than the minimum-utility requirement for carbon dioxide. In other words, hydrogen sulfide is the pinched component of the problem. Therefore, the network is synthesized based upon hydrogen sulfide. The generated network is identical to that illustrated in Figure 8. Then, each absorber is sized using Kremser's equation

$$\frac{y_p^{\text{out}} - m_{p,j}x_{p,j}^{\text{in}}}{y_p^{\text{in}} - m_{p,j}x_{p,j}^{\text{in}}} = \frac{1 - \left(\frac{L_j}{m_{p,j}G_i}\right)}{1 - \left(\frac{L_j}{m_{p,j}G_i}\right)^{N+1}} \tag{12}$$

where $N$ is the number of equilibrium stages in the absorber, and $L_j$, $G_i$ are the liquid and gas flow rates through the absorber, respectively. Hence, $N$ can be estimated for each of the four columns involved in the network. Then, Eq. 12 is used again together with the calculated number of stages for each column and the material balance equations to determine the composition of carbon dioxide throughout the network. The synthesized MEN is shown in Figure 10. The upper figures correspond to hydrogen sulfide whereas the lower correspond to carbon dioxide. Since the minimum-utility network for the pinched component (hydrogen sulfide) is capable of delivering the required separation duties for carbon dioxide, this MEN is one with compatible multicomponent targets.

## Conclusions

A systematic procedure that can cost-effectively solve the problem of synthesizing MEN's has been proposed. This procedure recognizes the pinch as the most constrained region of design. Thus, the network design ought to be started at the pinch and be developed by moving away from the pinch. The procedure also presents two feasibility criteria that identify the essential pinch matches and provide a rationale for stream splitting. Using the concepts of mass-load loops and paths, the designer can reduce the number of units at the expense of increasing the cost of MSA's. This results in a tradeoff between capital and operating costs. The proposed procedure applies to the synthesis of MEN's with single-component targets or multicomponent compatible targets.

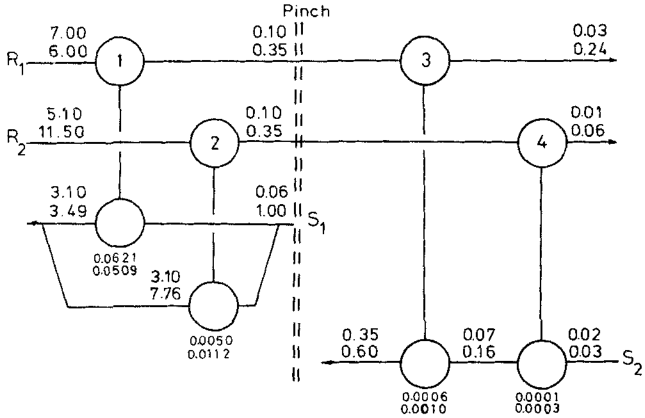


**Figure 10. A minimum-utility design for the simultaneous removal of hydrogen sulfide and carbon dioxide from COG.**

## Acknowledgment

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## Notation

$b_{p,j}$ = intercept of equilibrium line for component p in lean stream $j$
$E$ = index set of external MSA's
$G_i$ = mass flowrate of rich process stream $i$, kg/s
$i$ = index for rich streams
$j$ = index for lean streams
$L_j$ = mass flow rate of lean process stream $j$, kg/s
$m_{p,j}$ = slope of equilibrium line for component $p$ in lean stream $j$
$N$ = number of equilibrium stages in a mass exchanger
$n_{\text{int}}$ = number of composition intervals in the CIT
$N_i$ = number of independent problems in the network
$N_E$ = number of external MSA's
$N_R$ = number of rich streams
$N_S$ = number of lean process streams
$p$ = index for transferrable components
$P$ = set of transferrable components
$R$ = set of rich streams
$S$ = set of lean process streams
$U$ = minimum number of units
$U_{\text{MUD}}$ = minimum number of units compatible with a minimum-utility design
$x_{p,j}$ = mass fraction of the key component in lean stream $j$
$x_{p,j}^c$ = constrained outlet mass fraction of key component in lean stream $j$
$x_{p,j}^{\max}$ = maximum practically feasible outlet mass fraction of component $p$ in lean stream $j$
$x_{p,j}^s$ = supply mass fraction of component $p$ in lean stream $j$
$x_{p,j}^t$ = target mass fraction of component $p$ in lean stream $j$
$x_{p,j}^c$ = constrained outlet mass fraction of the key component in lean stream $j$
$y_p$ = mass fraction of component $p$ in any rich stream
$y_{p,i}^s$ = supply mass fraction of component $p$ in lean stream $i$
$y_{p,i}^t$ = target mass fraction of component $p$ in lean stream $i$

### *Subscripts*

$E$ = external MSA
$i$ = rich stream $i$
$j$ = lean stream $j$
$k$ = $k$th interval
$la$ = lean stream immediately above the pinch
$lb$ = lean stream immediately below the pinch
MUD = minimum-utility design
$P$ = transferrable component
$ra$ = rich stream immediately above the pinch
$rb$ = rich stream immediately below the pinch
$R$ = rich stream
$S$ = lean process stream

### *Superscripts*

$c$ = upper constrained value
max = maximum practically feasible
$s$ = supply
$t$ = target
$*$ = equilibrium

### *Greek letters*

$\Delta_{p,k}$ = surplus mass exchanged of component $p$ in interval $k$, kg/s
$\epsilon_{p,j}$ = minimum allowable composition difference for component $p$ in lean stream $j$

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