

CHAPTER FOUR

SYNTHESIS OF MASS EXCHANGE NETWORKS: A GRAPHICAL APPROACH

Mass-exchange units are among the most ubiquitous separation operations used in the process industries. A mass exchanger is any direct-contact mass-transfer unit that employs a mass separating agent “MSA” (or a lean stream) to selectively remove certain components (e.g., impurities, pollutants, byproducts, products) from a rich stream. The designation of a rich or a lean stream is not tied to the composition level of the components to be exchanged. Instead, the definition is task related. The stream from which the targeted components are removed is designated as the rich stream while the stream to which the targeted components are transferred is referred to as the lean stream (or MSA). The MSA should be partially or completely immiscible in the rich phase. Examples of mass exchange operations include absorption, adsorption, stripping, ion exchange, adsorption, solvent extraction, and leaching.

Multiple mass exchange units are typically used in a processing facility. Therefore, their collective selection, design, and operation must be coordinated and integrated. This chapter presents a systematic approach to the synthesis of networks involving multiple units of mass exchangers. First, the basics of mass-exchange equilibrium and design of individual units is addressed. Next, a graphical approach will be described to illustrate how a mass exchange network can be synthesized and how the multiple MSA’s and mass exchange technologies can be screened.

4.1. DESIGN OF INDIVIDUAL MASS EXCHANGERS

Consider the mass exchanger shown in Fig. 4.1. A certain component is transferred from the rich stream, i , to the lean stream, j . The rich stream has a flowrate, G_i , an inlet composition,

y_i^{in} , and an outlet composition, y_i^{out} . The lean stream has a flowrate, L_j , an inlet composition, x_j^{in} , and an outlet composition, x_j^{out} . Two important aspects govern the performance of a mass exchanger: *equilibrium function and material balance*.

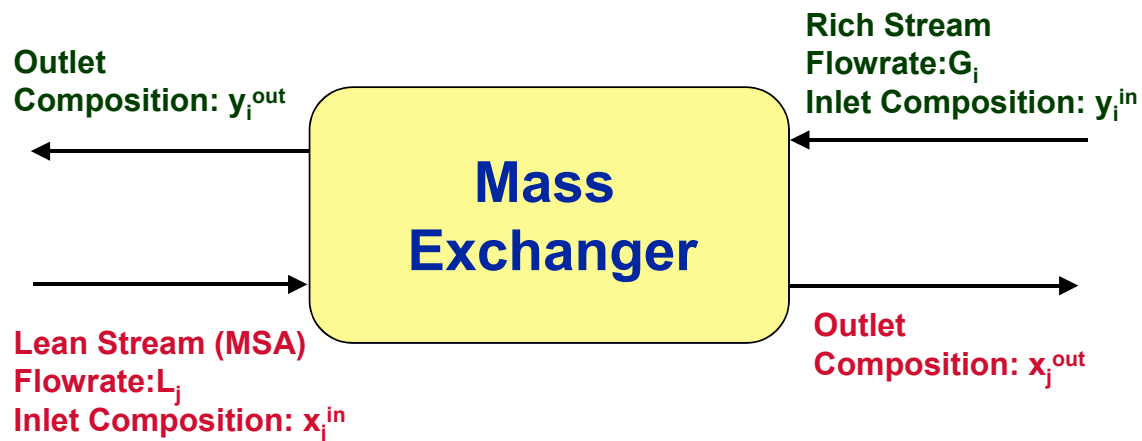


Fig. 4.1. A Generic Mass Exchanger

Equilibrium refers to the state at which there is no net interphase transfer of the targeted species (solute). This situation corresponds to the state at which both phases have the same value of chemical potential for the solute. Mathematically, the composition of the solute in the rich phase, y_i , can be related to its composition in the lean phase, x_j , via an equilibrium distribution function, f_j^* . Hence, for a given rich-stream composition, y_i , the maximum achievable composition of the solute in the lean phase, x_j^* , is given by

$$y_i = f_j^*(x_j^*) \quad (4.1)$$

Figure 4.2. is a schematic representation of an equilibrium function. In many cases, the equilibrium function can be linearized over a specific range of operation. As shown by Fig. 4.2, the linearized form has a slope of m_j and an intercept of b_j , i.e.

$$y_i = m_j x_j^* + b_j \quad (4.2)$$

There are several important special cases of Eq. (4.2) when the intercept, b_j , is zero. These include Henry's law, Raoult's law, and extraction equilibrium with distribution coefficients.

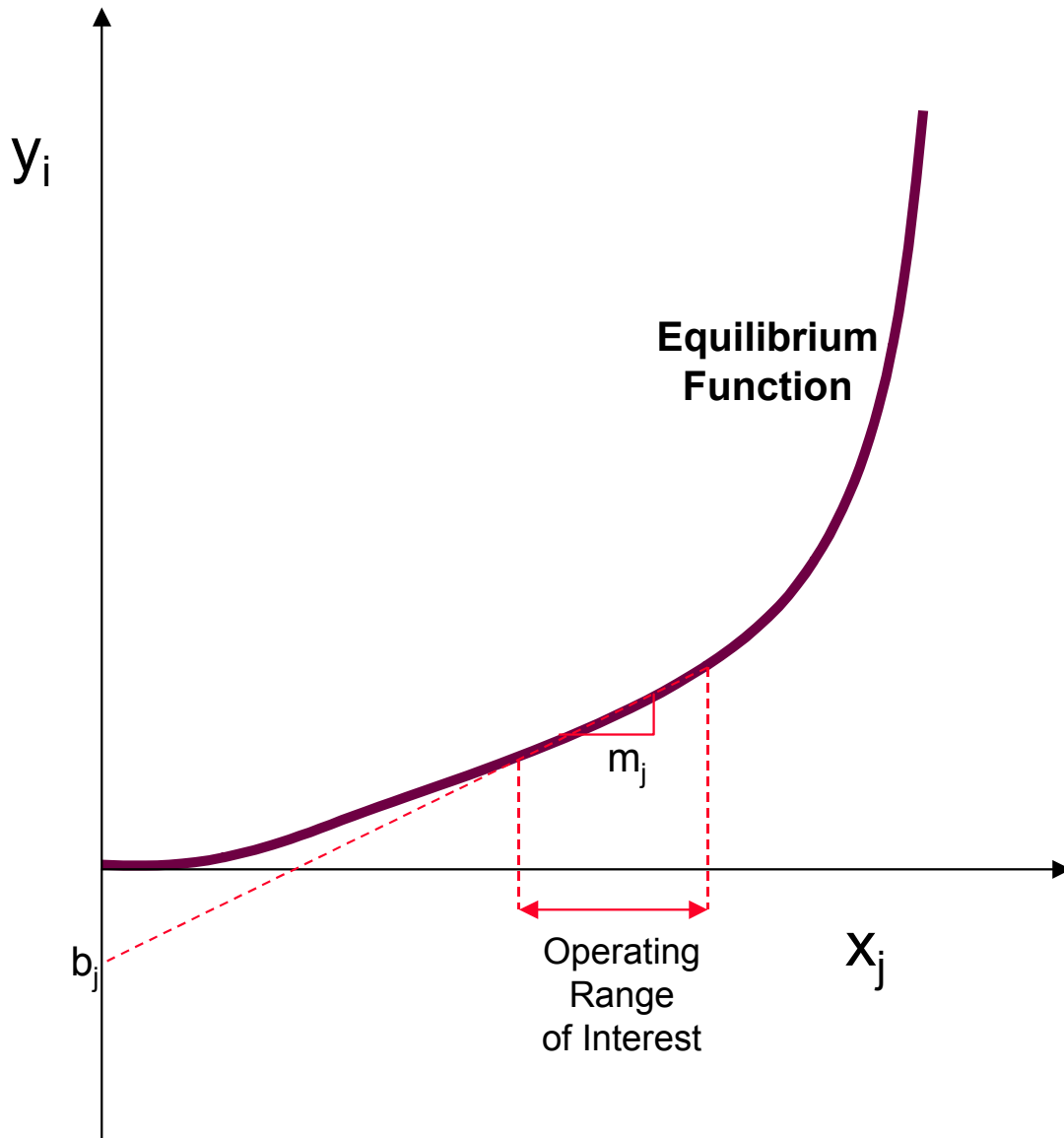


Fig. 4.2. Linearized Segment of Equilibrium Function

The material balance on the transferable solute accounts for the fact the mass of solute lost from the rich stream is equal to mass of solute gained by the lean stream, i.e.

$$G_i (y_i^{\text{in}} - y_i^{\text{out}}) = L_j (x_j^{\text{out}} - x_j^{\text{in}}) \quad (4.3)$$

The material balance equation provides the mathematical description of the *operating line*. The operating line can be graphically represented on a y - x (McCabe-Thiele) diagram. The operating line extends between the two terminal points $(y_i^{\text{in}}, x_j^{\text{out}})$ and $(y_i^{\text{out}}, x_j^{\text{in}})$ and has a slope of L_j/G_i , as shown in Fig. 4.3.

Mass exchangers may be broadly classified into two categories: *stagewise units* and *differential (continuous) contactors*. Stagewise units are characterized by discrete solute transfer where mass exchange takes place in a stage followed by disengagement between the rich and lean phases then mass exchange and so on. Examples of stagewise units include tray columns and multistage mixer-settler arrangements. An important concept in stagewise operations is the notion of an *equilibrium stage or a theoretical plate*. With sufficient mixing time, the two phases leaving the theoretical stage are essentially in equilibrium; hence the name equilibrium stage. A Each theoretical stage can be represented by a step between the operating line and the equilibrium line. Hence, the number of theoretical plates NTP can be determined by “stepping off” stages between the two ends of the exchanger, as shown by Fig. 4.3.

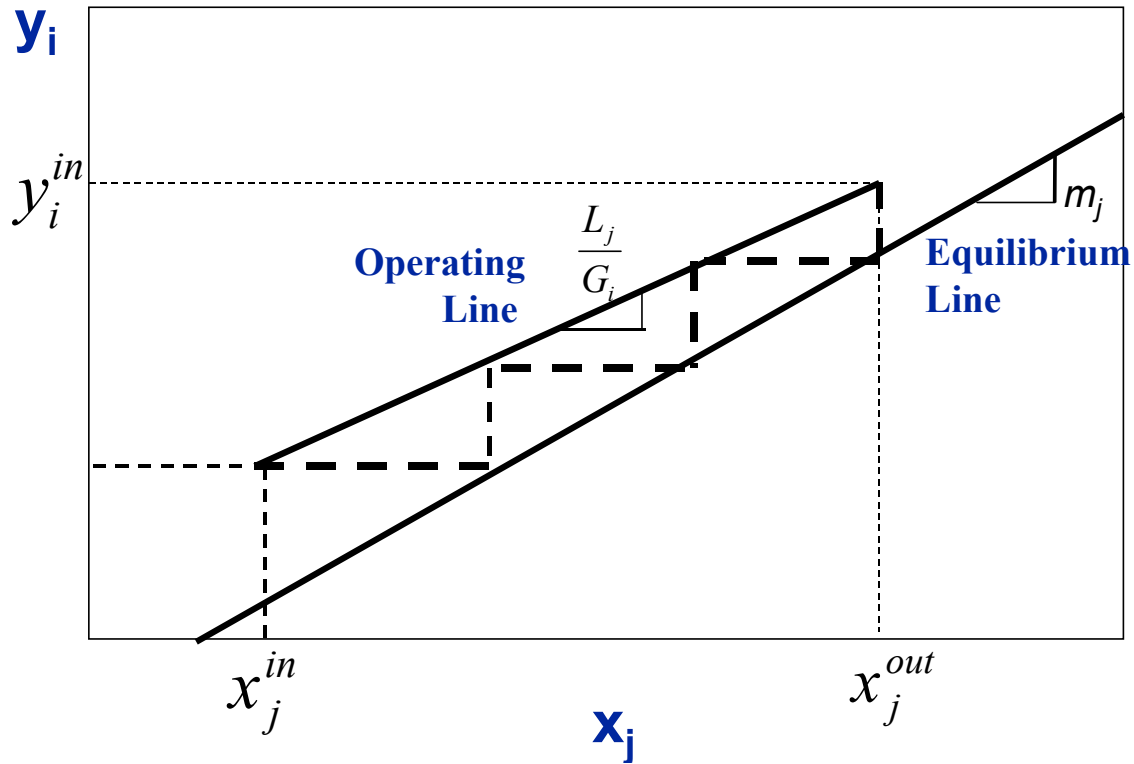


Fig. 4.3. The McCabe-Thiele Diagram for a Mass Exchanger

For the case of isothermal, dilute mass exchange with linear equilibrium, NTP can be determined through the Kremser (1930) equation:

$$NTP = \frac{\ln \left[\left(1 - \frac{m_j G_i}{L_j} \right) \left(\frac{y_i^{in} - m_j x_j^{in} - b_j}{y_i^{out} - m_j x_j^{in} - b_j} \right) + \frac{m_j G_i}{L_j} \right]}{\ln \left(\frac{L_j}{m_j G_i} \right)} \quad (4.4)$$

Other forms of the Kremser equation include

$$NTP = \frac{\ln \left[\left(1 - \frac{L_j}{m_j G_i} \right) \left(\frac{x_i^{in} - x_j^{out,*}}{x_j^{out} - x_j^{out,*}} \right) + \frac{L_i}{m_j G_i} \right]}{\ln \left(\frac{m_j G_i}{L_j} \right)} \quad (4.5)$$

where

$$x_j^{out,*} = \frac{y_i^{in} - b_j}{m_j} \quad (4.6)$$

Also,

$$\frac{y_i^{in} - m_j x_j^{out} - b_j}{y_i^{out} - m_j x_j^{in} - b_j} = \left(\frac{L_j}{m_j G_i} \right)^{NTP} \quad (4.7)$$

Other expressions for the number of theoretical plates avoiding logarithmic terms (for mathematical programming purposes) can also be found in literature (Fraser and Shenoy, 2004; Szitkai et al., 2002).

Equilibrium requires long-enough (infinite) contact time between the two phases. Therefore, to relate actual performance to equilibrium behavior it is necessary to calculate the number of actual plates “NAP” by incorporating contacting efficiency. A common method to account for efficiency is to use an overall exchanger efficiency, η_o , which can be used to relate NAP and NTP as follows

$$NAP = NTP / \eta_o \quad (4.8)$$

Once the number of plates is determined, the height of the mass exchanger can be determined by allowing a plate spacing distance between each two consecutive plates. The column diameter is normally determined by selecting a superficial velocity for one (or both) of the phases. This velocity is intended to ensure proper mixing while avoiding hydrodynamic problems such as flooding, weeping, or entrainment. Once a superficial velocity is determined, the cross-sectional area of the column is obtained by dividing the volumetric flowrate by the velocity.

Continuous (differential) mass exchanger include packed units, spray exchangers, and bubble columns. The height of a differential contactor, H , may be estimated using

$$H = HTU_y NTU_y \quad (4.9a)$$

$$= HTU_x NTU_x \quad , \quad (4.9b)$$

where HTU_y and HTU_x are the overall height of transfer units based on the rich and the lean phases, respectively, while NTU_y and NTU_x are the overall number of transfer units based on the rich and the lean phases, respectively.

The overall height of a transfer unit may be provided by the packing (or unit) manufacturer or estimated using empirical correlations (typically by dividing superficial velocity of one phase by its overall mass transfer coefficient). On the other hand, the number of transfer units can be theoretically estimated for the case of isothermal, dilute mass exchangers with linear equilibrium as follows:

$$NTU_y = \frac{y_i^{in} - y_i^{out}}{(y_i - y_i^*)_{\log mean}}, \quad (4.10a)$$

where

$$(y_i - y_i^*)_{\log mean} = \frac{(y_i^{in} - m_j x_j^{out} - b_j) - (y_i^{out} - m_j x_j^{in} - b_j)}{\ln \left(\frac{y_i^{in} - m_j x_j^{out} - b_j}{y_i^{out} - m_j x_j^{in} - b_j} \right)} \quad (4.10b)$$

and

$$NTU_x = \frac{x_j^{in} - x_j^{out}}{(x_j - x_j^*)_{\log mean}}, \quad (4.11a)$$

where

$$(x_j - x_j^*)_{\log mean} = \frac{\left[x_j^{out} - \left(\frac{y_i^{in} - b_j}{m_j} \right) \right] - \left[x_j^{in} - \left(\frac{y_i^{out} - b_j}{m_j} \right) \right]}{\ln \left\{ \frac{\left[x_j^{out} - \left(\frac{y_i^{in} - b_j}{m_j} \right) \right]}{\left[x_j^{in} - \left(\frac{y_i^{out} - b_j}{m_j} \right) \right]} \right\}}. \quad (4.11b)$$

If the terminal compositions or L_j/G_i are unknown, it is convenient to use the following form:

$$NTU_y = \frac{\ln \left[\left(1 - \frac{m_j G_i}{L_j} \right) \left(\frac{y_i^{in} - m_j x_j^{in} - b_j}{y_i^{out} - m_j x_j^{in} - b_j} \right) + \frac{m_j G_i}{L_j} \right]}{1 - \left(\frac{m_j G_i}{L_j} \right)}. \quad (4.12)$$

4.2. COST OPTIMIZATION OF MASS EXCHANGERS

In assessing the economics of a mass exchanger, two types of cost must be considered: fixed and operating. The *fixed cost (investment)* refers to the cost of the mass exchanger (e.g., shell, trays, etc.), ancillary devices (e.g., pump, compressor), installation, insulation, instrumentation, electric work, piping, engineering work and construction. Fixed capital investments are characterized by the fact that have to be replaced after a number of years commonly referred to as service life or useful life period because of wear and tear or by virtue of becoming obsolete or inefficient. Therefore, it is useful to evaluate an annual cost associated with the capital investment of the mass exchanger, referred to as the *annualized fixed cost* “*AFC*”. A simplified method for evaluating AFC is to consider the initial fixed cost of the equipment (FC_o) and its salvage value (FC_s) after n years of useful life period. Using an annual depreciation scheme, we get

$$AFC = \frac{FC_o - FC_s}{n} \quad (4.13)$$

In addition to the fixed capital investment needed to purchase and install the mass-exchange system and auxiliaries, there is a continuous expenditure referred to as operating cost which is needed to operate the mass exchanger. The operating cost includes mass-separating agents (makeup, regeneration, etc.) and utilities (heating, cooling, etc.).

By combining the fixed and operating costs, we get the total annualized cost of a mass-exchange system:

$$\text{Total annualized cost} = \text{Annualized fixed cost} + \text{Annual operating cost} \quad (4.14)$$

In order to minimize TAC, it is necessary to trade off the fixed cost versus the operating cost. Such tradeoffs can be established by identifying the role of the mass-exchange driving force between the actual operation and the equilibrium limits. In order to reach equilibrium compositions, an infinitely-large mass exchanger is required. Therefore, the operating line must have a positive

driving force with respect to the equilibrium line. The minimum driving force between the operating line and the equilibrium line is referred to as the *minimum allowable composition difference* and is designated by ε_j as shown by Fig. 4.4.

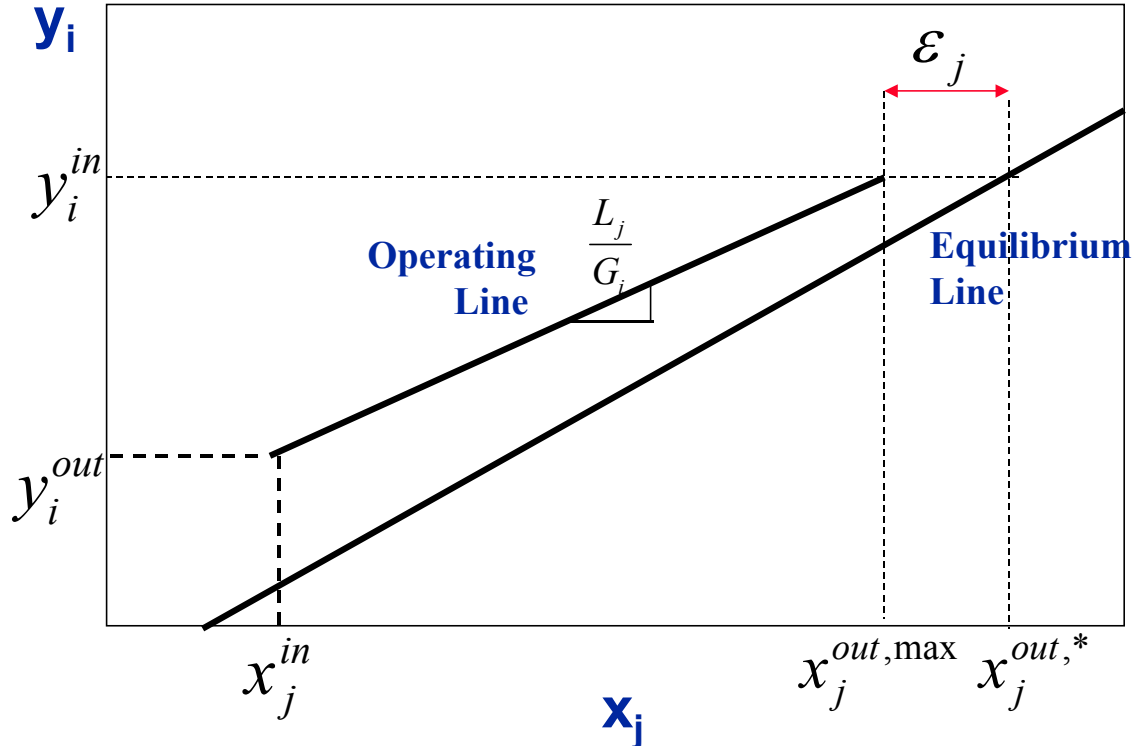


Fig. 4.4. Establishing a Minimum Allowable Composition Difference

The minimum allowable composition difference can be used to tradeoff capital versus operating costs. In order to demonstrate this concept, let us consider the mass exchanger represented on the y-x diagram of Fig. 4.4. For the rich stream, the inlet and outlet compositions as well as the flowrate are all given. For the lean stream, the inlet composition is given while the flowrate and the outlet compositions are unknown. Hence, the operating line described by Eq. (4.3)

has two unknowns: x_j^{out} and L_j . The maximum theoretically attainable outlet composition in the lean phase ($x_j^{out,*}$) is the equilibrium value corresponding to the inlet composition of the rich stream (Fig. 4.4). As mentioned earlier, achieving this equilibrium value requires an infinitely-large mass exchanger. Once the minimum allowable composition difference is selected, the maximum practically feasible outlet composition in the lean stream ($x_j^{out,max}$) can be determined as:

$$x_j^{out,max} = x_j^{out,*} - \varepsilon_j \quad (4.15)$$

but

$$y_i^{in} = m_j x_j^{out,*} + b_j \quad (4.16)$$

Combining Eqs. (4.15) and (4.16), one obtains

$$x_j^{out,max} = \frac{y_i^{in} - b_j}{m_j} - \varepsilon_j \quad (4.17)$$

To examine the effect of ε_j on the cost of the mass exchanger, let us assess the effect of selecting two values of the minimum allowable composition difference: ε_1 and ε_2 (Fig. 4.5). As ε_j increases, the slope of the operating line increases and the flowrate of the MSA increases leading to an increase in the operating cost of the mass exchanger. Meanwhile, as ε_j increases the number of theoretical plates decreases thereby leading to a reduction in the fixed cost. By varying ε_j and evaluating the corresponding annualized fixed cost, annual operating cost, and total annualized cost, we can determine the optimum value of minimum allowable composition difference, $\varepsilon_j^{Optimum}$, which corresponds to the minimum total annualized cost (Fig. 4.6). It is also worth noting that when ε_j is

set to zero, the annualized fixed cost is infinity while the annual operating cost is at its minimum value.

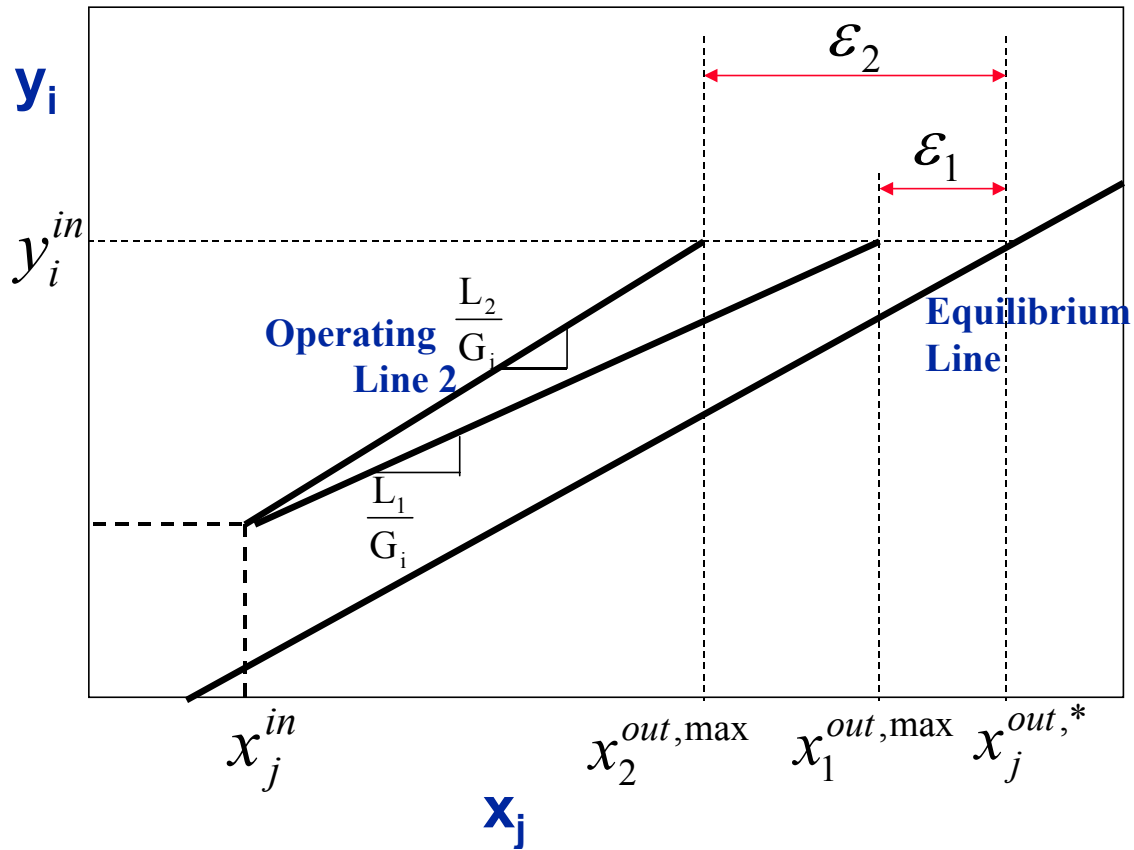


Fig. 4.5. Changing Minimum Allowable Composition Difference

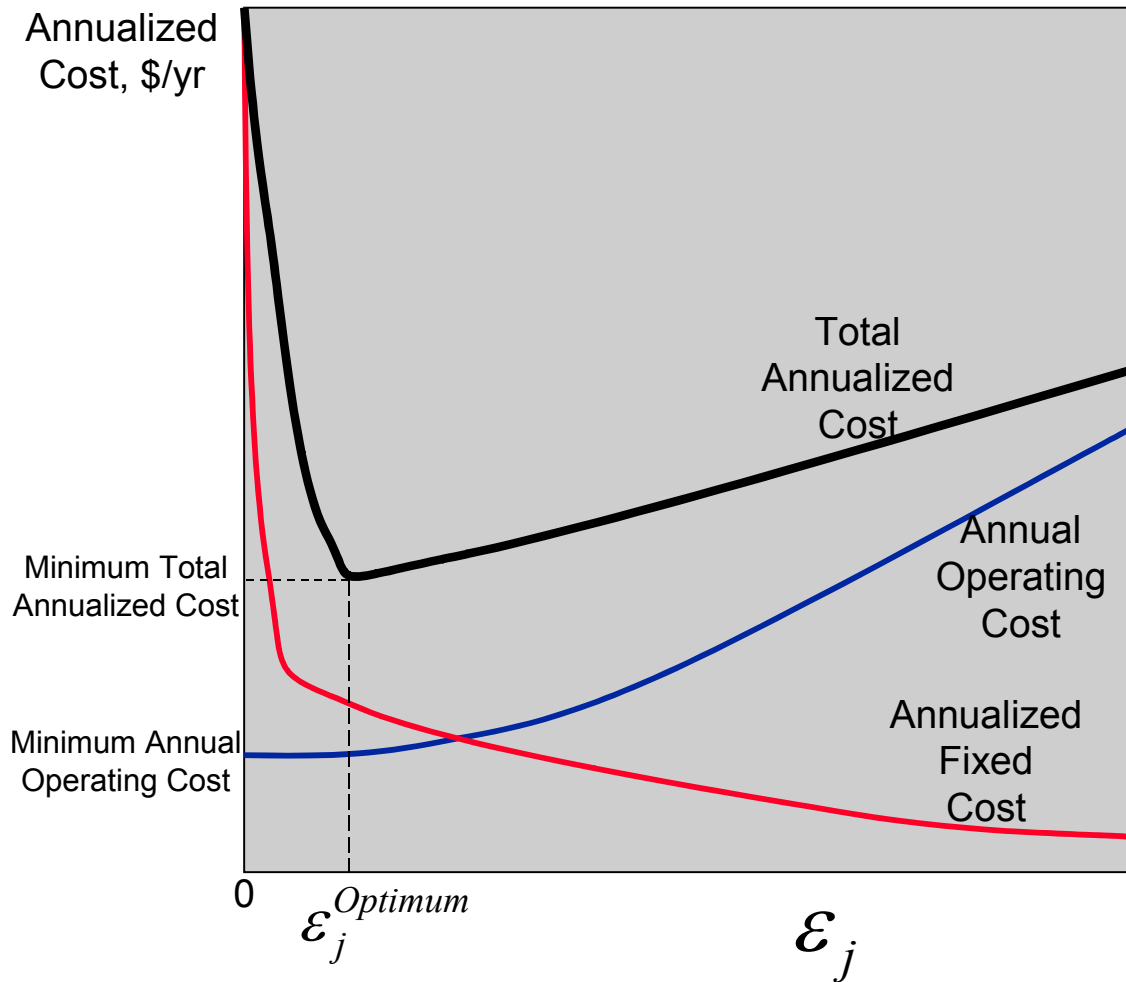


Fig. 4.6. Selection of Optimum Minimum Allowable Composition Difference

The foregoing analysis can be used to incorporate thermodynamic and economic issues into practical-feasibility constraints. To demonstrate this concept, let us consider a mass exchanger for which the equilibrium relation governing the transfer of the solute from the rich stream, i , to the MSA, j , is given by the linear expression

$$y_i = m_j x_j^* + b_j, \quad (4.18)$$

which indicates that for a rich stream composition of y_i , the maximum theoretically attainable composition of the MSA is x_j^* . By employing a minimum allowable composition difference of ϵ_j ,

one can draw a "practical-feasibility line" that is parallel to the equilibrium line but offset to its left by a distance ε_j (Fig. 4.7). Therefore, the lean-stream composition on the practical feasibility line can be mathematically represented as:

$$x_j^{\max} = x_j^* - \varepsilon_j \quad (4.19)$$

i.e.,

$$x_j^{\max} = \frac{y_i - b_j}{m_j} - \varepsilon_j \quad (4.20a)$$

or

$$y_i = m_j(x_j^{\max} + \varepsilon_j) + b_j \quad (4.20b)$$

In order for an operating line to be practically feasible, it must lie in the region to the left of the practical-feasibility line. Hence, for any point lying on the practical-feasibility line, two statements can be made. For a given \bar{y}_i , the value x_j^{\max} corresponds to the maximum composition of the solute that is practically achievable in the MSA. Therefore, the solute can be practically transferred from \bar{y}_i to x_j^{\max} or any lean-stream composition lower than x_j^{\max} (lies to its left on the graph). Conversely, for a given x_j^{\max} , the value \bar{y}_i corresponds to the minimum composition of the solute in the rich stream that is needed to practically transfer the solute from the rich stream to the MSA. Therefore, the solute can be transferred to x_j^{\max} from \bar{y}_i or any higher rich-stream composition. These two aspects are shown by Fig. 4.8.

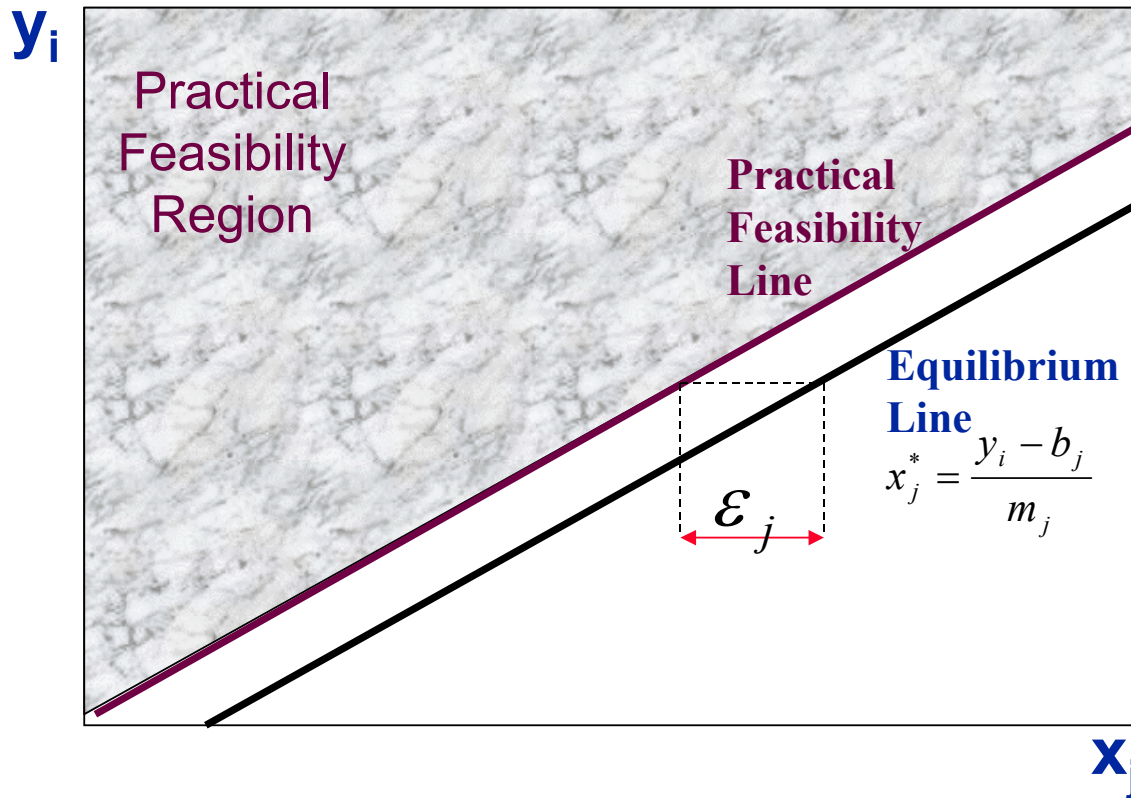


Fig. 4.7. Establishing the Practical Feasibility Region

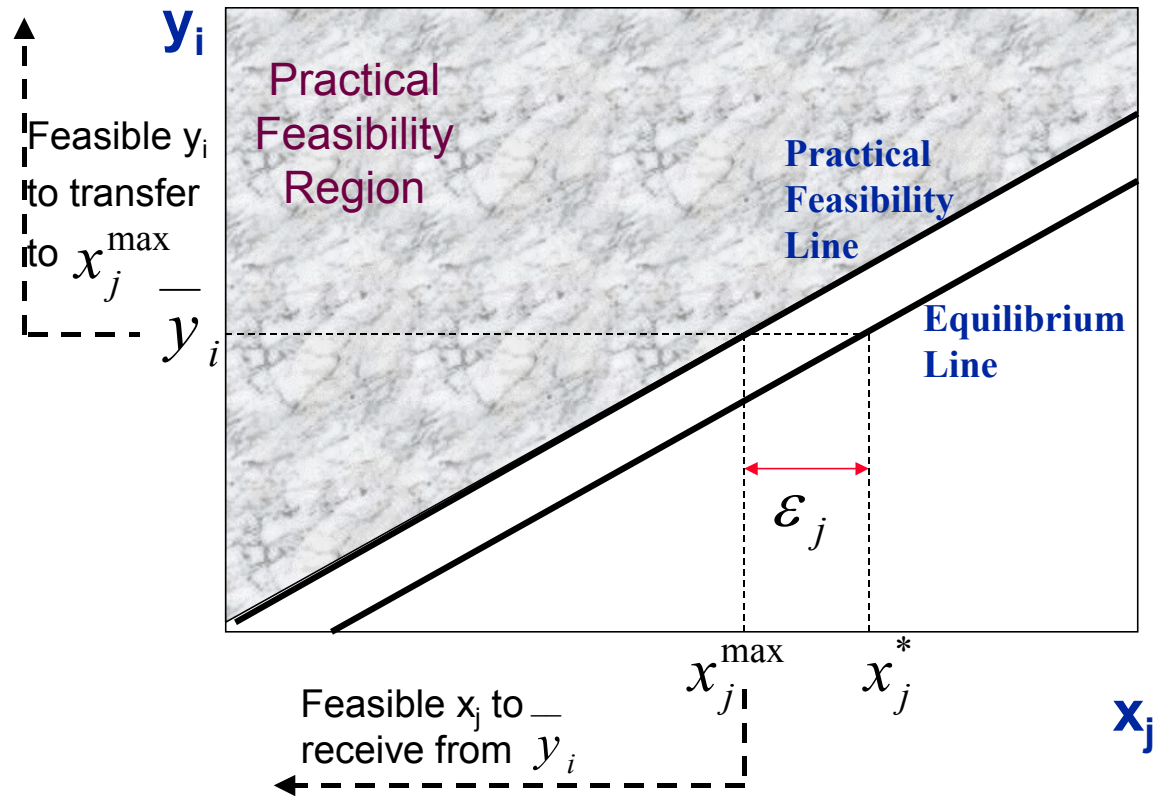


Fig. 4.8. Identifying Practically-Feasible Composition Regions

EXAMPLE 4.1. BENZENE RECOVERY FROM A GASEOUS EMISSION (El-Halwagi, 1997)

Benzene is to be removed from a gaseous emission by contacting it with an absorbent (wash oil, molecular weight 300). The gas flowrate is 0.2 kg-mole/s (about 7,700 ft³/min) and it contains 0.1 mol/mol % (1000 ppm) of benzene. The molecular weight of the gas is 29, its temperature is 300 K, and it has a pressure of 141 kPa (approximately 1.4 atm). It is desired to reduce the benzene content in the gas to 0.01 mol/mol % using the system shown in Fig. 4.9. Benzene is first absorbed into oil. The oil is then fed to a regeneration system in which oil is

heated and passed to a flash column that recovers benzene as a top product. The bottom product is the regenerated oil, which contains 0.08 mol/mol % benzene. The regenerated oil is cooled and pumped back to the absorber.

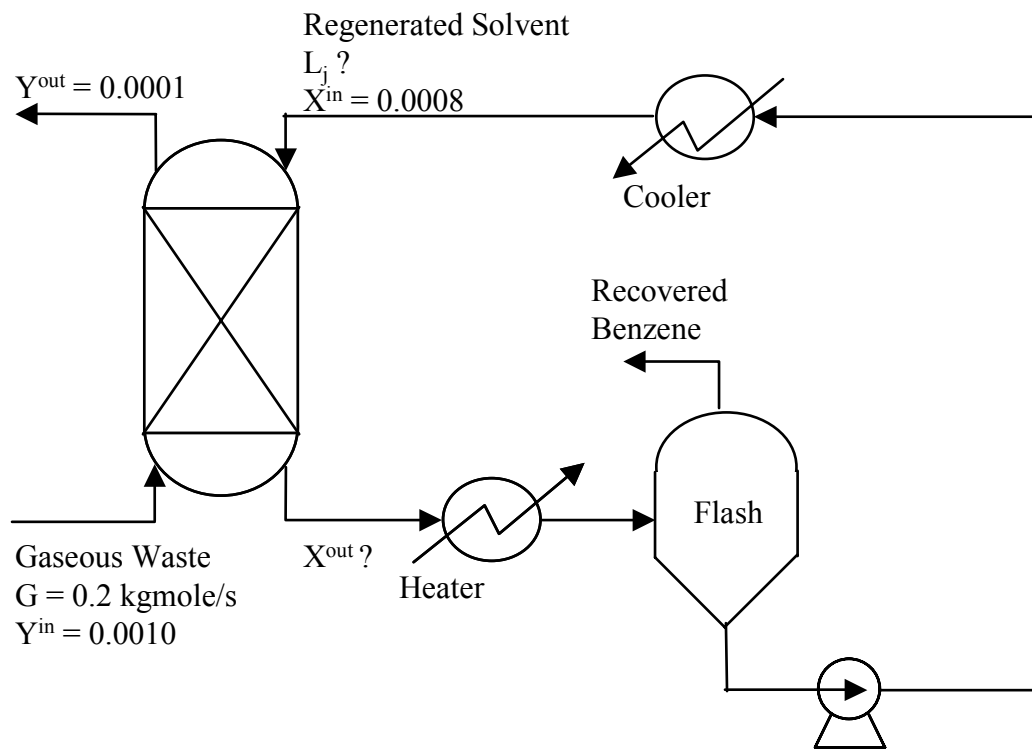


Fig. 4.9. Benzene Recovery Process

What is the optimal flowrate of recirculating oil that minimizes the TAC of the system?

The following data may be used

Equilibrium Data

- The absorption operation is assumed to be isothermal (at 300 K) and to follow Raoult's law:

$$y = \left(\frac{P^0}{P^{Total}} \right) x \quad (4.21)$$

where y is the mole fraction of benzene in air and x is the mole fraction of benzene in oil.

- The vapor pressure of benzene, p^0 , is given by:

$$\ln p^0 = 20.8 - \frac{2789}{T - 52} \quad (4.22)$$

where p^0 is in Pascals and T is in Kelvins.

Absorber Sizing Criteria

- The overall-gas height of transfer unit for the packing is 0.6 m.
- The superficial velocity of the gas in the absorber is taken as 1.5 m/s to avoid flooding.
- The mass velocity of oil in the absorber should be kept above 2.7 kg/m².s to insure proper wetting.

Cost Information

- The operating cost (including pumping, oil makeup, heating and cooling) is \$0.05/kg-mole of recirculating oil.
- The system is to be operated for 8,000 hrs/annum.
- The installed cost, \$, of the absorption column (including auxiliaries, but excluding packing) is given by

$$\text{Installed cost of column} = 2,300 H^{0.85} D^{0.95} , \quad (4.23)$$

where H is the packing height (m) and D is the column diameter (m).

- The packing cost is \$800/m³ (4.24)
- The oil-regeneration system is to be salvaged from a closing unit in the plant. Hence, its fixed cost will not be accounted for in the optimization calculations.
- The absorber and packing are assumed to depreciate linearly over five years with negligible salvage values.

Solution

At 300 K, the vapor pressure of benzene can be calculated from Eq. (4.22):

$$\ln p^o = 20.8 - \frac{2,789}{300 - 52} \quad (4.25a)$$

i.e.,

$$p^o = 14,101 \text{ Pa} \quad (4.25b)$$

Since the system is assumed to follow Raoult's law, then Eq.(4.21) can be used to give

$$m = \frac{14,101}{141,000} \quad (4.26)$$

$$\approx 0.1 \frac{\text{mole fraction of benzene in air}}{\text{mole fraction of benzene in oil}}$$

As has been previously mentioned, the minimum TAC can be identified by iteratively varying ϵ . Since the inlet and outlet compositions of the rich stream as well as the inlet composition of the MSA are fixed, one can vary ϵ at the rich end of the exchanger (and consequently the outlet composition of the lean stream) to minimize the TAC of the system. In

order to demonstrate this optimization procedure, let us first select a value of ε at the rich end of the exchanger equal to 1.5×10^{-3} and evaluate the system size and cost for this value.

Outlet Composition of Benzene in Oil:

Let us set the outlet mole fraction of benzene in oil equal to its maximum practically feasible value given by Eqs.(4.15) and (4.16) . Since the intercept (b) in this case is zero, we get:

$$x^{out} = \frac{y^{in}}{m} - \varepsilon \quad (4.27a)$$

$$\begin{aligned} x^{out} &= \frac{10^{-3}}{0.1} - 1.5 \times 10^{-3} \\ &= 8.5 \times 10^{-3}. \end{aligned} \quad (4.27b)$$

Flowrate of Oil:

A component material balance on benzene gives

$$L (8.5 \times 10^{-3} - 8 \times 10^{-4}) = 0.2 (10^{-3} - 10^{-4}) \quad (4.28a)$$

or

$$L = 0.0234 \text{ kg mol/s} \quad (4.28b)$$

Operating Cost:

$$\begin{aligned} \text{Annual operating cost} &= 0.05 \frac{\$}{\text{kgmoleoil}} \times 0.0234 \frac{\text{kgmoleoil}}{\text{s}} \times 3600 \times 8000 \frac{\text{s}}{\text{yr}} \\ &= \$33,700/\text{yr} \end{aligned} \quad (4.29)$$

Column Height:

According to Eq.(4.10b)

$$\begin{aligned}
 (y - y^*)_{\log \text{ mean}} &= \frac{(10^{-3} - 0.1 \times 8.5 \times 10^{-3})(10^{-4} - 0.1 \times 8 \times 10^{-4})}{\ln\left(\frac{10^{-3} - 0.1 \times 8.5 \times 10^{-3}}{10^{-4} - 0.1 \times 8 \times 10^{-4}}\right)} \\
 &= 6.45 \times 10^{-5}
 \end{aligned}
 \tag{4.30}$$

Therefore, NTU_y can be calculated using Eq.(4.10a) as

$$\begin{aligned}
 NTU_y &= \frac{10^{-3} - 10^{-4}}{6.45 \times 10^{-5}} \\
 &= 13.95
 \end{aligned}
 \tag{4.31}$$

and the height is obtained from Eq.(4.9a)

$$\begin{aligned}
 H &= 0.6 \times 13.95 \\
 &= 8.37 \text{ m}
 \end{aligned}
 \tag{4.32}$$

Column Diameter

$$D = \sqrt{\frac{4 \times \text{Volumetric Flowrate of Gas}}{\pi \text{ Gas Superficial Velocity}}}
 \tag{4.33}$$

But

$$\begin{aligned}
 \text{Molar density of gas} &= \frac{P}{RT} \\
 &= \frac{141}{8.3143 \times 300} \\
 &= 0.057 \text{ kgmole/m}^3
 \end{aligned}
 \tag{4.34}$$

Therefore,

$$\begin{aligned}
 \text{Volumetric flowrate of gas} &= \frac{0.2 \frac{\text{kgmole}}{\text{s}}}{0.057 \frac{\text{kgmole}}{\text{m}^3}} \\
 &= 3.51 \text{ m}^3 / \text{s}
 \end{aligned}
 \tag{4.35}$$

and

$$\begin{aligned}
 D &= \sqrt{\frac{4 \times 3.51}{3.14 \times 1.5}} \\
 &= 1.73 \text{ m.}
 \end{aligned}
 \tag{4.36}$$

It is worth pointing out that the mass velocity of oil is

$$\frac{0.0234 \frac{\text{kgmole}}{\text{s}} \times \frac{300\text{kg}}{\text{kgmole}}}{\frac{\pi}{4}(1.73)^2} \approx 3\text{kg/s}
 \tag{4.37}$$

which is acceptable since it is greater than the minimum wetting velocity ($2.7 \frac{\text{kg}}{\text{m}^2 \text{ s}}$).

Fixed Cost

$$\begin{aligned}
 \text{Fixed cost of installed shell and auxiliaries} &= 2,300 (8.37)^{0.85} (1.73)^{0.95} \\
 &= \$23,600
 \end{aligned}
 \tag{4.38}$$

$$\begin{aligned}
 \text{Cost of packing} &= (800) \frac{\pi}{4} (1.73)^2 (8.37) \\
 &= \$15,700
 \end{aligned}
 \tag{4.39}$$

Total Annualized Cost

$$\begin{aligned}
 \text{TAC} &= \text{annual operating cost} + \text{annualized fixed cost} \\
 &= 33,700 + \frac{(23,600 + 15,700)}{5} \\
 &= \$41,560 / \text{yr}
 \end{aligned}
 \tag{4.40}$$

This procedure is carried out for various values of ε until the minimum TAC is identified. The results shown in Fig. 4.10 indicate that the value of $\varepsilon = 1.5 \times 10^{-3}$ used in the preceding calculations is the optimum one leading to a minimum TAC of \$41,560 /yr.

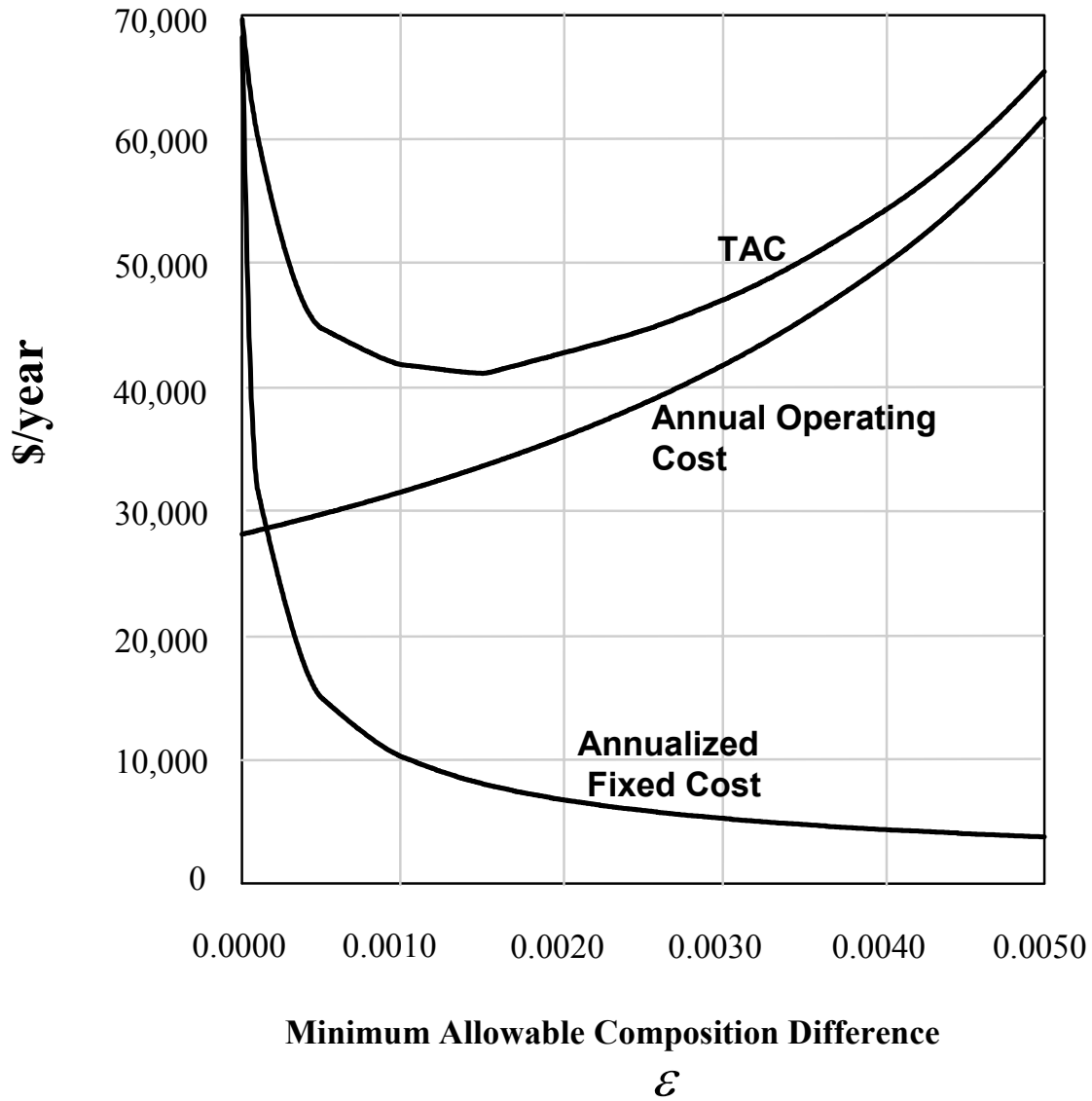


Fig. 4.10. Cost Minimization for the Benzene Recovery Mass-Exchange Process

4.3. PROBLEM STATEMENT FOR SYNTHESIS OF MASS-EXCHANGE NETWORKS

In many processing facilities, mass exchangers are used to separate targeted species from a number of rich streams. More than one mass-exchange technology and more than one MSA may be considered. In such situations, it is necessary to integrate the decisions and design of the multiple mass exchangers. This requires a holistic approach to consider all separation tasks from all rich stream, simultaneously screen all candidate mass exchange operations and MSAs, and identify the optimum network of mass exchangers. El-Halwagi and Manousiouthakis (1989) introduced the problem of synthesizing *mass-exchange network* “**MENs**” and developed systematic techniques for their optimal design. The problem of synthesizing MENs can be stated as follows: Given a number N_R of rich streams (sources) and a number N_S of MSAs (lean streams), it is desired to synthesize a cost- effective network of mass exchangers that can preferentially transfer certain species from the rich streams to the MSAs. Given also are the flowrate of each rich stream, G_i , its supply (inlet) composition y_i^s , and its target (outlet) composition y_i^t , where $i = 1, 2, \dots, N_R$. In addition, the supply and target compositions, x_j^s and x_j^t , are given for each MSA, where $j = 1, 2, \dots, N_S$. The flowrate of each MSA is unknown and is to be determined so as to minimize the network cost. Figure 4.11 is a schematic representation of the MEN problem statement.

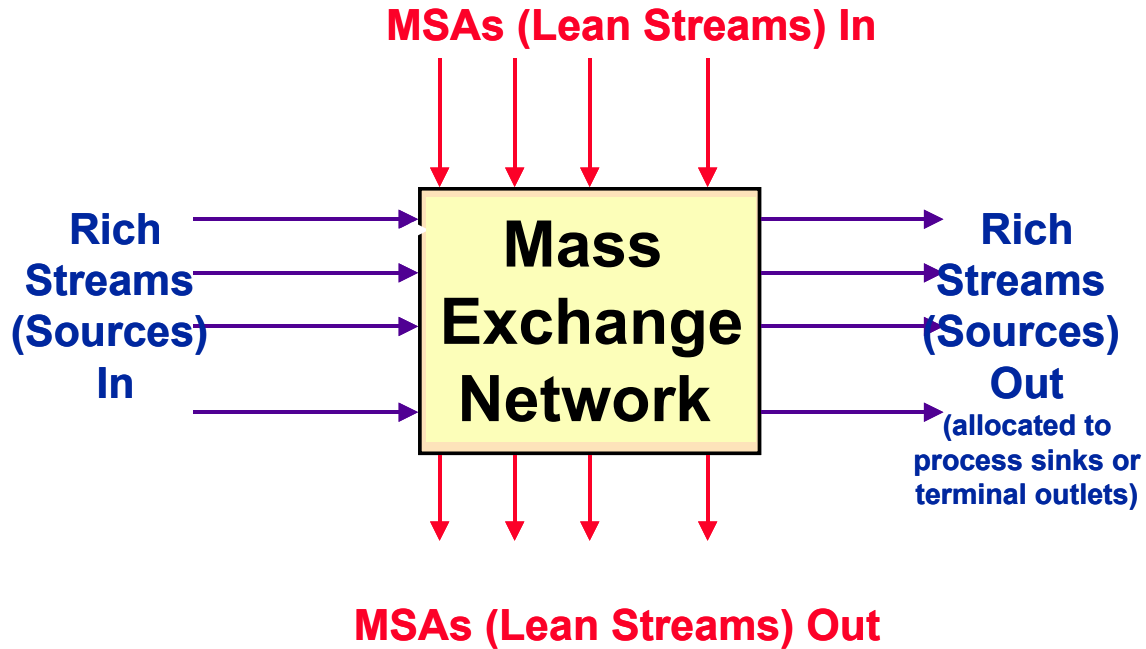


Figure 4.11. Schematic representation of the MEN synthesis problem. (El-Halwagi and Manousiouthakis, 1989a)

The candidate lean streams can be classified into N_{SP} process MSAs and N_{SE} external MSAs (where $N_{SP} + N_{SE} = N_S$). The process MSAs already exist on plant site and can be used for the removal of the undesirable species at a very low cost (virtually free). The flowrate of each process MSA that can be used for mass exchange is bounded by its availability in the plant, i.e.,

$$L_j \leq L_j^c \quad j = 1, 2, \dots, N_{SP} \quad (4.41)$$

where L_j^c is the flowrate of the j^{th} MSA that is available in the plant. On the other hand, the external MSAs can be purchased from the market. Their flowrates are to be determined according to the overall economic considerations of the MEN.

Typically, rich streams leaving the MEN are either allocated to process sinks (equipment) or assigned to be terminal streams (e.g., products, wastes). When the outlet rich streams are allocated to process sinks, the target composition of the rich stream are selected so as to satisfy the constraints on the feed to these sinks. In case of final discharge, the target composition of the undesirable species in each rich stream corresponds to the environmental regulations. Finally, if the outlet rich stream corresponds to a terminal product, the target composition is set to satisfy quality requirements for the product.

The target composition of the in each MSA is an upper bound on the actual outlet composition of the MSA. The value of the target composition is selected based on a number of factors whose nature may be:

- Physical (e.g., saturation compositions, solubility limits, precipitation conditions)
- Operational: If the outlet MSA is used in a subsequent unit, its content of certain species must conform to the constraints on the feed to the subsequent unit
- Safety (e.g., to stay away from flammability/explosion limits)
- Health (e.g., to avoid reaching toxic compositions)
- Environmental (e.g., to satisfy emission regulations)
- Economic (e.g., to minimize the cost of the mass-exchange and regeneration systems such as Example 4.1)
- Technical feasibility (e.g., to satisfy thermodynamic constraints and minimum driving force such as Eq. 4.17)

The MEN synthesis task entails answering several design questions and challenges:

- Which mass-exchange technologies should be utilized (e.g., adsorption, solvent extraction ion exchange, etc.)?
- Which MSAs should be selected (e.g., which solvents, adsorbents)?
- What is the optimal flowrate of each MSA?
- How should these MSAs be matched with the rich streams?
- What is the optimal system configuration (e.g., how should these mass exchangers be arranged? Is there any stream splitting and mixing?) ?

In responding to these questions, one must consider the numerous (infinite) number of alternative solutions. Instead of attempting an exhaustive enumeration technique (which would be hopelessly complicated), it is necessary to extract the optimum solution from among the numerous alternatives without enumeration or trial and error. The next section presents an integrated method to the synthesis of MENs referred to as the mass-exchange pinch analysis.

4.4. MASS-EXCHANGE PINCH DIAGRAM

The mass exchange pinch analysis (El-Halwagi and Manousiouthakis, 1989) provides a holistic and systematic approach to synthesizing MENs. It also enables the identification of rigorous targets such as minimum cost of MSAs. The first step in the analysis is to develop an integrated view of all the separation tasks for the rich streams. This can be achieved by developing a composite representation of mass exchanged from all the rich streams. Mass of targeted species removed from the i^{th} rich stream is given by:

$$MR_i = G_i (y_i^s - y_i^t), \quad i=1,2,\dots,N_R. \quad (4.42)$$

By plotting mass exchanged versus composition, each rich stream is represented as an arrow whose tail corresponds to its supply composition and its head to its target composition. The slope of each arrow is equal to the stream flowrate. The vertical distance between the tail and the head of each arrow represents the mass of targeted species that is lost by that rich stream. In this representation, the vertical scale is only relative. Any stream can be moved up or down while preserving the same vertical distance between the arrow head and tail and maintaining the same supply and target compositions. A stream cannot be moved left or right, otherwise stream composition will be altered. A convenient way of vertically placing each arrow is to rank the rich streams in ascending order of their targeted composition then we stack the rich streams on top of one another, starting with the rich stream having the lowest target composition. Once the first rich stream is represented, we draw a horizontal line passing through the arrow tail of the stream. Next, the second rich stream is represented as an arrow extending between its supply and target compositions and having a vertical distance equal to the mass of the targeted species to be removed from this stream. The arrowhead of the second rich stream is placed on the horizontal line passing through the arrow tail of the first rich stream. The procedure is continued for all the rich streams (Fig. 4.12).

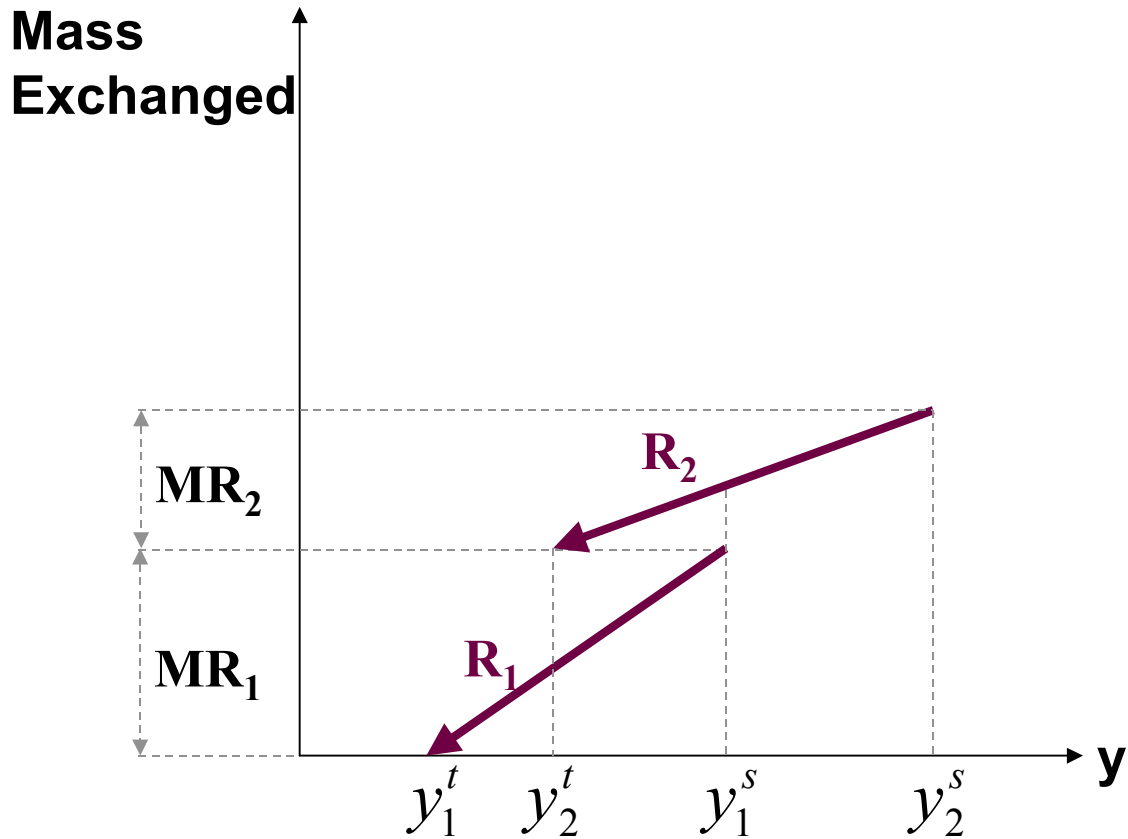


Fig. 4.12. Representation of mass exchanged by two rich streams.

After all the rich streams have been represented, it is necessary to develop a combined representation of the rich streams that allows us to observe the separation tasks of all rich streams as a function of composition. A rich composite stream can be constructed using "diagonal rule" for superposition to add up mass in the overlapped regions of streams (Fig. 4.13). In the region between y_1^t and y_2^t , there is only R_1 . Therefore, the composite representation is exactly the same as R_1 . Similarly, in the region between y_1^s and y_2^s there is only R_2 and, hence, the composite representation is exactly the same as R_2 . In the overlapping region of the two rich streams (between y_2^t and y_1^s), the

composite representation of the two streams is the diagonal (hence the name diagonal rule). By connecting these three linear segments, we now have a rich composite stream which represents the cumulative mass of the targeted species removed from all the rich streams. It captures the relevant characteristics of the rich streams and enables the simultaneous consideration of all rich streams and developing an integrated mass-exchange strategy for all of them.

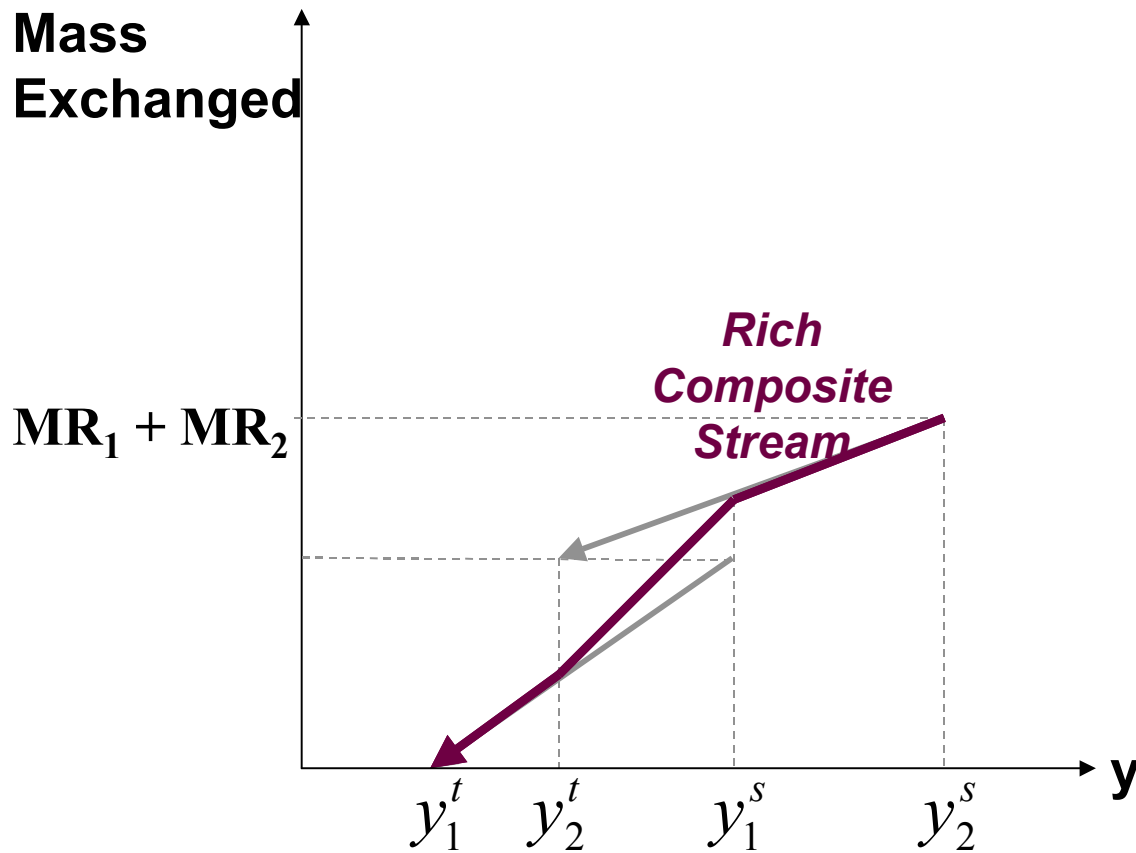


Fig. 4.13. Constructing a rich composite stream using superposition

Next, attention is turned to the lean streams. Since the process MSAs are available on-site and may be used virtually for no or little operating cost, we will first consider maximizing their use. The remaining load will then be removed using external MSAs. Therefore, we first establish N_{SP} lean composition scales (one for each process MSA) that are in one-to-one correspondence with the rich scale according to the Eq. (4.20). Next, the mass of targeted species that can be gained by each process MSA is plotted versus the composition scale of that MSA. Hence, each process MSA is represented as an arrow extending between supply and target compositions (see 4.14 for a two-MSA example). The vertical distance between the arrow head and tail is given by

Mass of solute that can be gained by the j^{th} process MSA

$$MS_j = L_j^c (x_j^t - x_j^s) \quad j = 1, 2, \dots, N_{SP}. \quad (4.43)$$

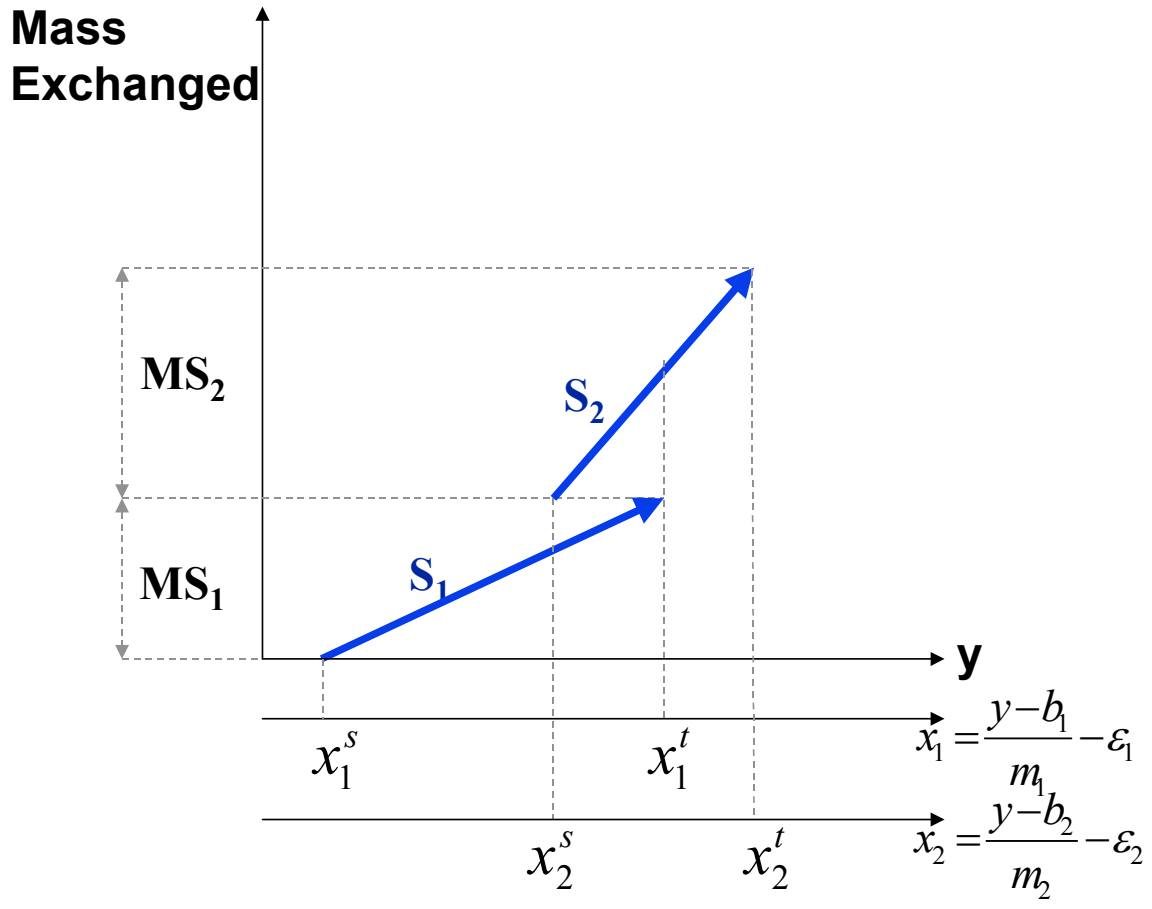


Fig. 4.14. Representation of mass exchanged by two process MSAs.

Once again, the vertical scale is only relative and any stream can be moved up or down on the diagram. A convenient way of vertically placing each arrow is to stack the process MSAs on top of one another starting with the MSA having the lowest supply composition (Fig. 4.15). Hence, a lean composite stream representing the cumulative mass of the targeted species gained by all the MSAs is obtained by using the diagonal rule for superposition.

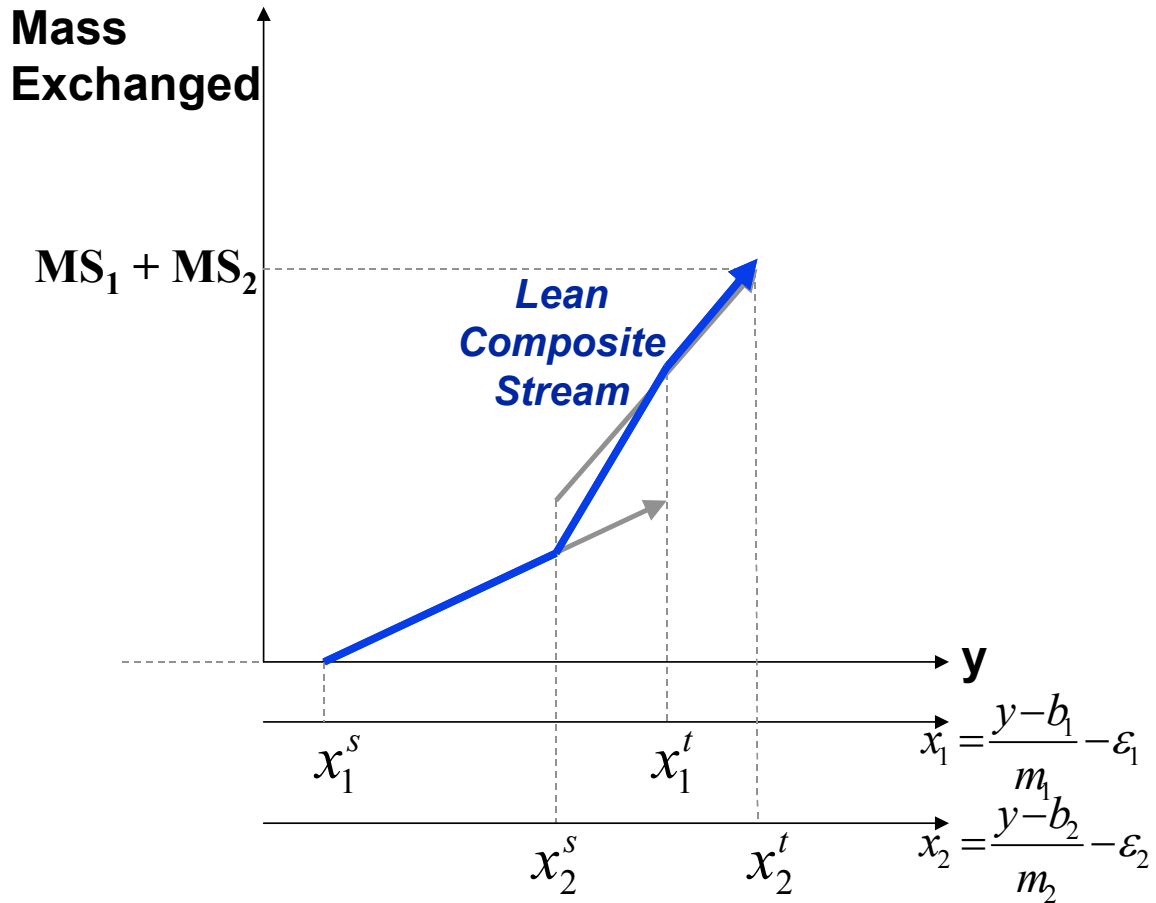


Fig. 4.15. Construction of the lean composite stream using superposition.

Next, both composite streams are plotted on the same diagram (Fig. 4.16). On this diagram, thermodynamic feasibility of mass exchange is guaranteed when at any mass-exchange level (which corresponds to a horizontal line), the composition of the lean composite stream is located to the left of the rich composite stream. Because of the use of Eq. (4.20) in mapping the composition scales, when mass is transferred to the left, constraints on thermodynamics as well as the minimum driving force are satisfied. For a given set of corresponding composition scales $\{y, x_1, x_2, \dots, x_j, \dots, x_{NS}\}$ it is thermodynamically and practically feasible to transfer the targeted species from any rich stream to

any MSA. In addition, it is also feasible to transfer the targeted species from any rich stream of a composition y_i to any MSA which has a composition less than the x_j obtained from.

The lean composite stream can be moved up and down which implies different mass-exchange decisions. For instance, if we move the lean composite stream upwards in a way that leaves no horizontal overlap with the rich composite stream, then there is no integrated mass exchange between the rich composite stream and the process MSAs as seen in Fig. 4.16. When the lean composite stream is moved downwards so as to provide some horizontal overlap (Fig. 4.17), some integrated mass exchange can be achieved. The remaining load of the rich composite stream has to be removed by the external MSAs. However, if the lean composite stream is moved downwards such that a portion of the lean is placed to the right of the rich composite stream, thereby creating infeasibility (Fig. 4.18). Therefore, the optimal situation is constructed when the lean composite stream is slid vertically until it touches the rich composite stream while lying completely to the left of the rich composite stream at any horizontal level. The point where the two composite streams touch is called the "mass-exchange pinch point"; hence the name "pinch diagram" (Fig. 4.19).

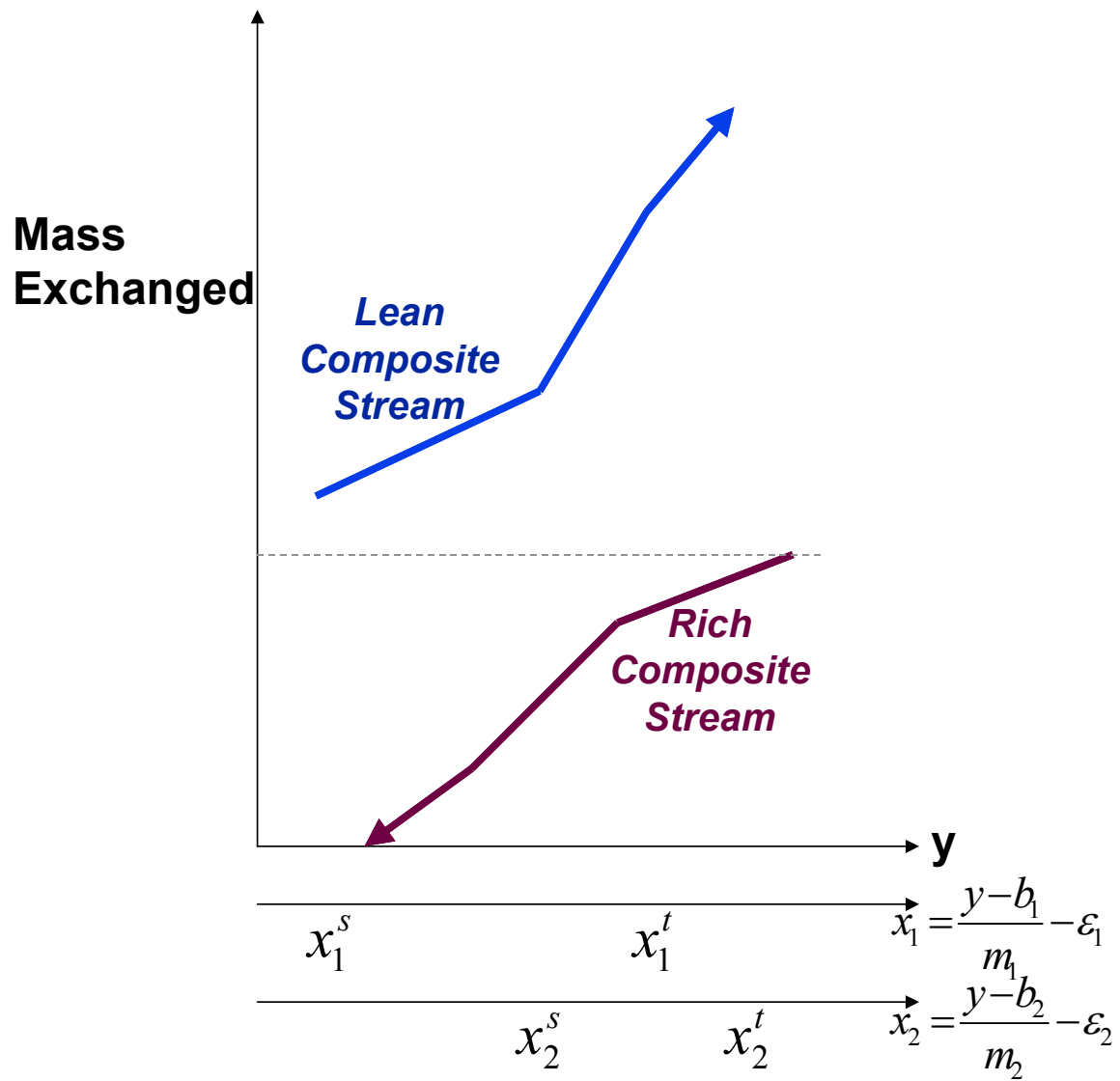


Fig. 4.16. No Integration between Rich and Process MSAs

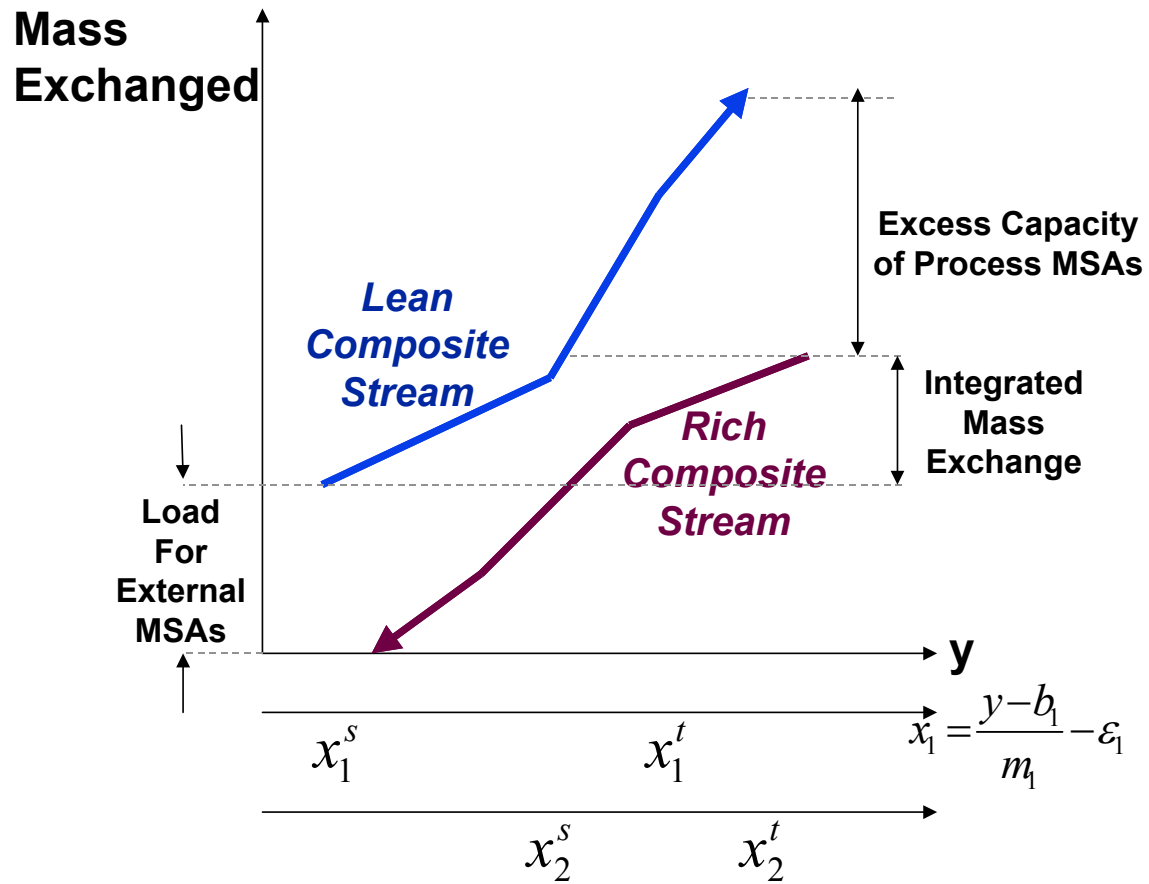


Fig. 4.17. Partial Integration of Rich and Lean Streams (Passing Mass through the Pinch)

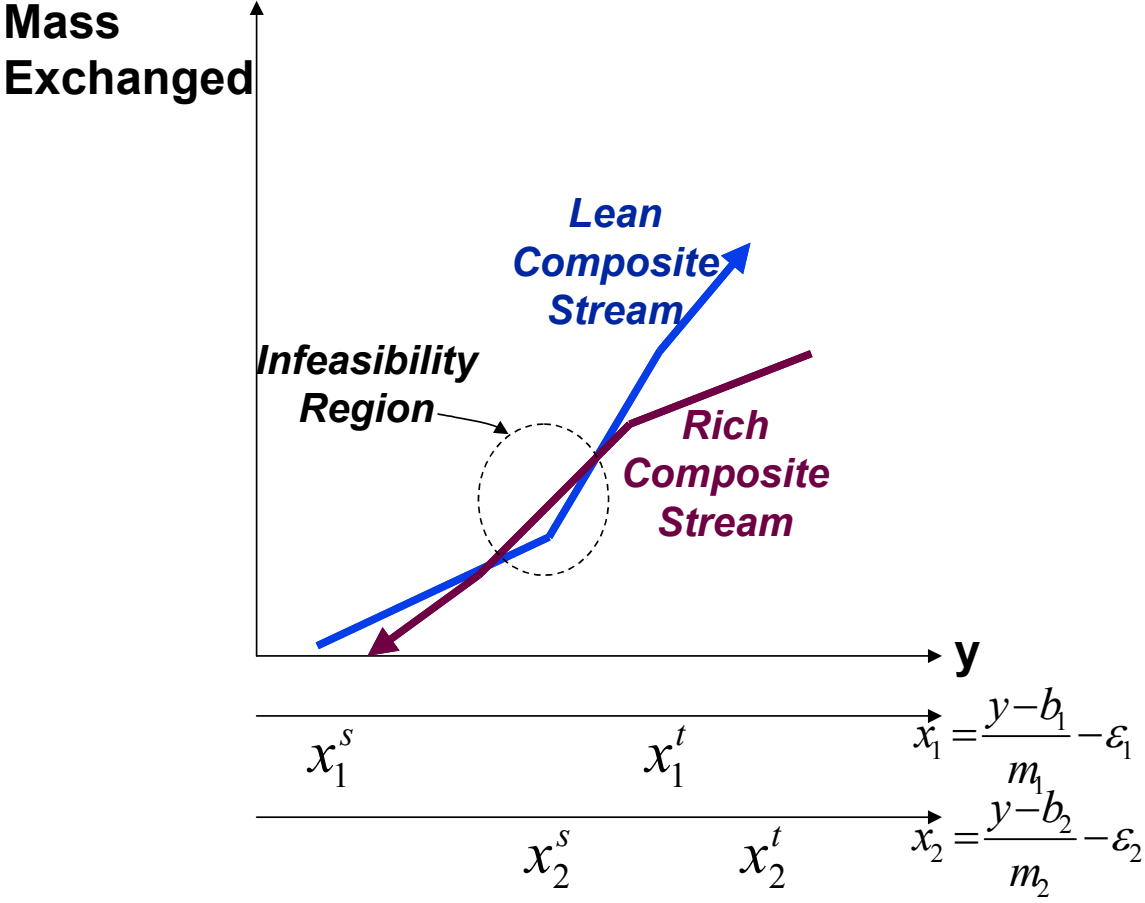


Fig. 4.18 Causing Infeasibility by Placing Lean to the Rich of Rich

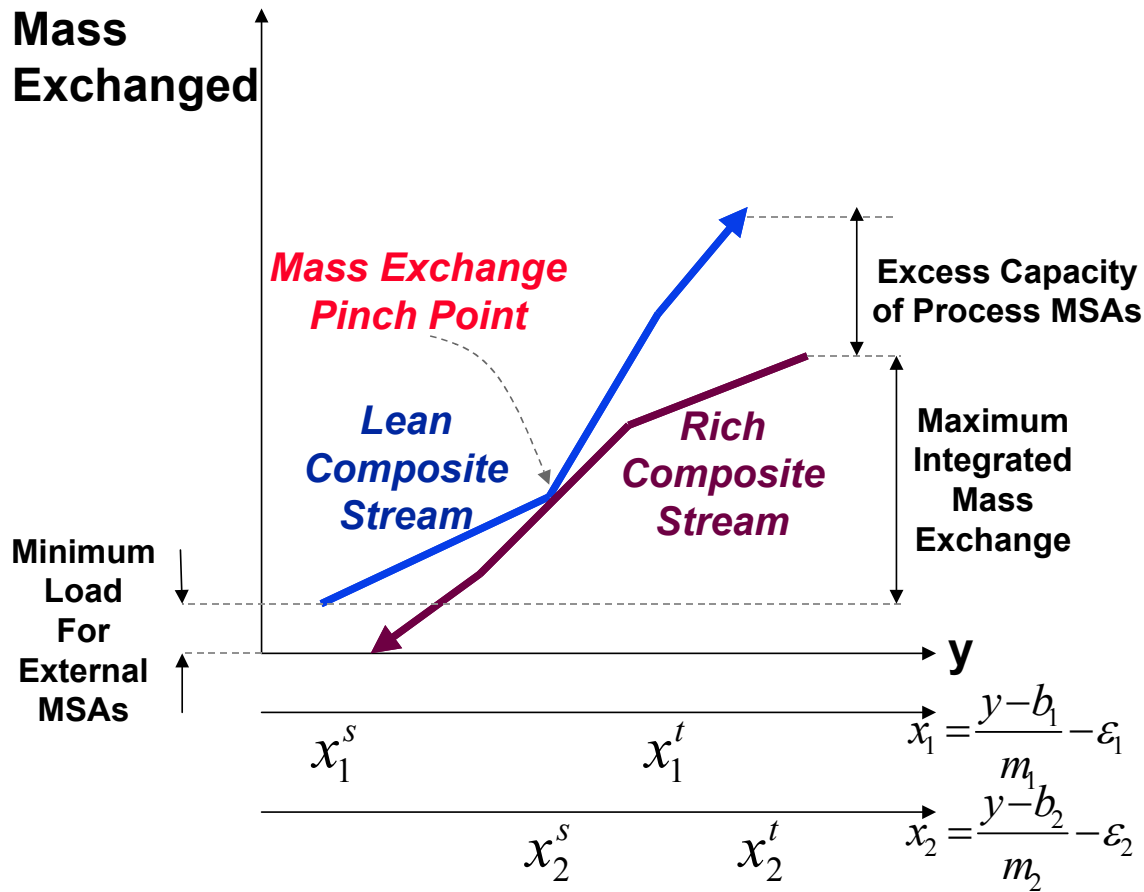


Fig. 4.19. The Mass-Exchange Pinch Diagram.

On the pinch diagram, the vertical overlap between the two composite streams represents the maximum amount of the targeted species that can be transferred from the rich streams to the process MSAs. It is referred to as the "integrated mass exchange." The vertical distance of the lean composite stream which lies above the upper end of the rich composite stream is referred to as "excess process MSAs." It corresponds to that capacity of the process MSAs to remove the targeted species that cannot be used because of thermodynamic infeasibility. According to the designer's preference or to the specific circumstances of the process such excess can be eliminated from service

by lowering the flowrate and/or the outlet composition of one or more of the process MSAs. Finally, the vertical distance of the waste composite stream which lies below the lower end of the lean composite stream corresponds to the mass of the targeted species to be removed by external MSAs. These targets have been identified rigorously using little data and without detailing the design of the MEN.

The above discussion indicates that in order to achieve the targets for maximum integration of mass exchange from rich stream to process MSAs and minimum load to be removed by the external MSAs, the following ***three design rules*** are needed:

- *No mass should be passed through the pinch (i.e. the two composites must touch)*
- *No excess capacity should be removed from MSA's below the pinch*
- *No external MSAs should be used above the pinch*

. Above the pinch, exchange between the rich and the lean process streams takes place. External MSAs are not required. Using an external MSA above the pinch will incur a penalty eliminating an equivalent amount of process lean streams from service. On the other hand, below the pinch, both the process and the external lean streams should be used. Furthermore, Fig. 4.17 indicates that if any mass is transferred across the pinch, the composite lean stream will move upward and, consequently, external MSAs in excess of the minimum requirement will be used. Therefore, to minimize the cost of external MSAs, mass should not be transferred across the pinch. It is worth pointing out that these observations are valid only for the class of MEN problems covered in this chapter. When the assumptions employed in this chapter are relaxed, more general conclusions can be made. For instance, it will be shown later that the pinch analysis can still be undertaken even when there are no process MSAs in the plant.

EXAMPLE 4.2. SYNTHESIZING A NETWORK OF MASS EXCHANGERS FOR BENZENE RECOVERY (El-Halwagi, 1997)

Figure 4.20 shows a simplified flowsheet of a copolymerization plant. The copolymer is produced via a two-stage reaction. The monomers are first dissolved in a benzene-based solvent. The mixed-monomer mixture is fed to the first stage of reaction where a catalytic solution is added. Several additives (extending oil, inhibitors, and special additives) are mixed in a mechanically stirred column. The resulting solution is fed to the second-stage reactor, where the copolymer properties are adjusted. The stream leaving the second-stage reactor is passed to a separation system which produces four fractions: copolymer, unreacted monomers, benzene, and gaseous waste. The copolymer is fed to a coagulation and finishing section. The unreacted monomers are recycled to the first-stage reactor, and the recovered benzene is returned to the monomer-mixing tank. The gaseous waste, R_1 , contains benzene as the primary pollutant that should be recovered. The stream data for R_1 are given in Table 4.1.

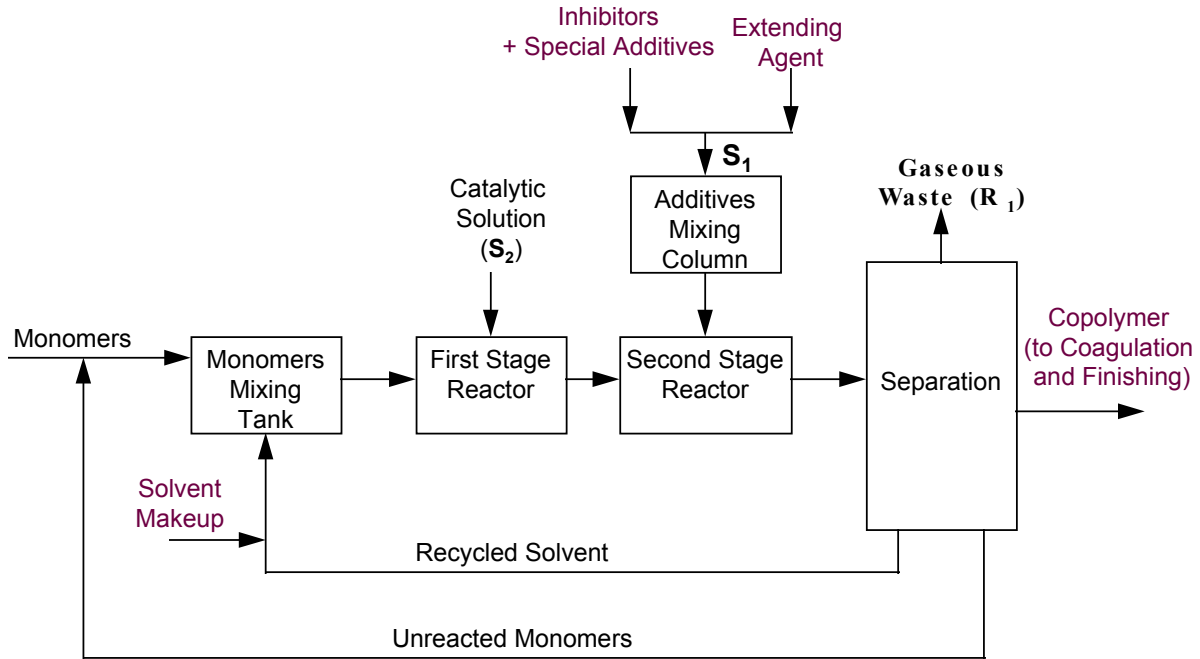


Fig. 4.20. A Simplified flowsheet of a copolymerization process.

Table 4.1. Data of Waste Stream for the Benzene Removal Example

Stream	Description	Flowrate G_b , kg mol/s	Supply composition (mole fraction) y_i^s	Target composition (mole fraction) y_i^t
R_1	Off-gas from product separation	0.2	0.0020	0.0001

Two process MSAs and one external MSA are considered for recovering benzene from the gaseous waste. The two process MSAs are the additives, S_1 , and the liquid catalytic solution, S_2 . They can be used for benzene recovery at virtually no operating cost. In addition to its

positive environmental impact, the recovery of benzene by these two MSAs offers an economic incentive since it reduces the benzene makeup needed to compensate for the processing losses. Furthermore, the additives mixing column can be used as an absorption column by bubbling the gaseous waste into the additives. The mixing pattern and speed of the mechanical stirrer can be adjusted to achieve a wide variety of mass-transfer tasks. The stream data for S_1 and S_2 are given in Table 4.2. The equilibrium data for benzene in the two process MSAs are given by:

$$y_1 = 0.25x_1 \quad (4.44)$$

and

$$y_1 = 0.50x_2, \quad (4.45)$$

where y_1 , x_1 and x_2 are the mole fractions of benzene in the gaseous waste, S_1 and S_2 respectively. For control purposes, the minimum allowable composition difference for S_1 and S_2 should not be less than 0.001.

Table 4.2. Data of Process Lean Streams for the Benzene Removal Example

Stream	Description	Upper bound on flowrate L_j^c kg mol/s	Supply composition of benzene (mole fraction) x_j^s	Target composition of benzene (mole fraction) x_j^t
S_1	Additives	0.08	0.003	0.006
S_2	Catalytic solution	0.05	0.002	0.004

The external MSA, S_3 , is an organic oil that can be regenerated using flash separation. The operating cost of the oil (including pumping, makeup, and regeneration) is \$0.05/kg mol of recirculating oil. The equilibrium relation for transferring benzene from the gaseous waste to the oil is given by

$$y_1 = 0.10x_3. \quad (4.46)$$

The data for S_3 are given in Table 4.3. The absorber sizing equations and fixed cost were given in Example 4.2. Using the graphical pinch approach, synthesize a cost-effective MEN that can be used to remove benzene from the gaseous waste (Fig. 4.21).

Table 4.3. Data for the External MSA for the Benzene Removal Example

Stream	Description	Upper Bound on Flowrate L_j^c kgmole/s	Supply Composition of Benzene (mole fraction) x_j^s	Target Composition of Benzene (mole fraction) x_j^t
S_3	Organic Oil	?	0.0008	0.0100

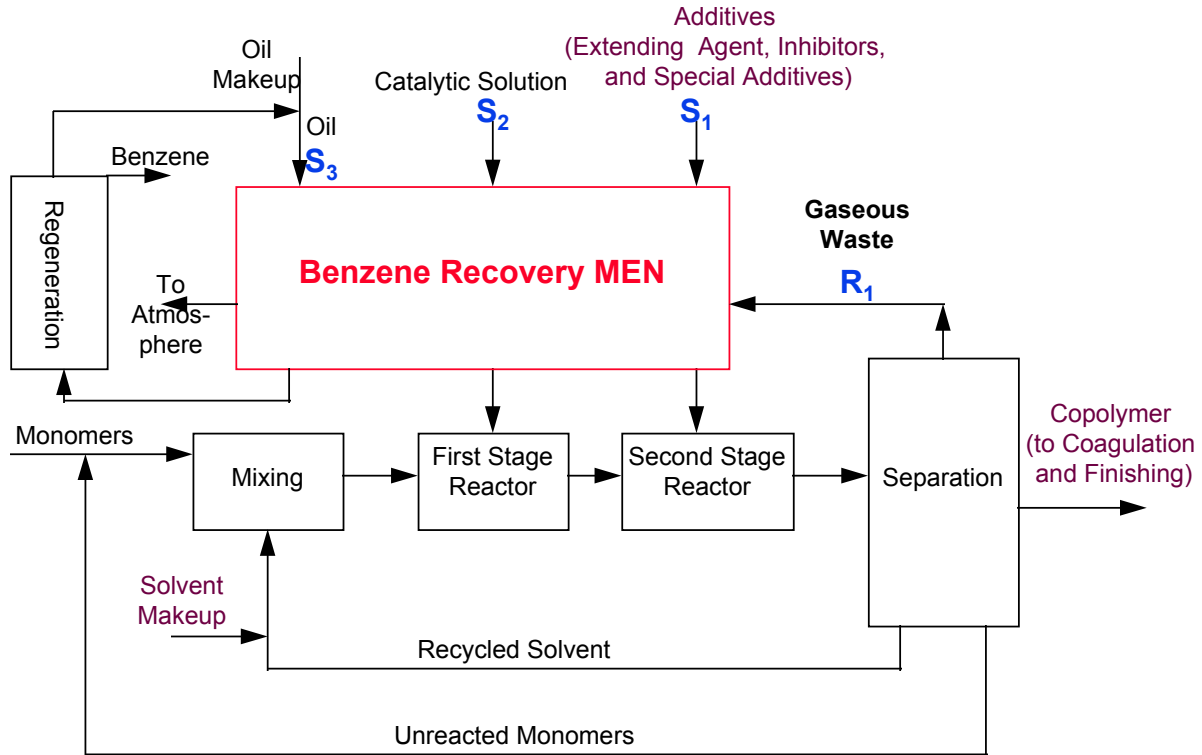


Fig. 4.21. The copolymerization process with a benzene recovery MEN.

Solution

Constructing the Pinch Diagram

As has been described earlier, the rich composite stream is first plotted as shown in Fig. 4.22. Next, the lean composite stream is constructed for the two process MSAs. Equation (4.20) is employed to generate the correspondence among the composition scales y , x_1 and x_2 . The least permissible values of the minimum allowable composition difference are used ($\varepsilon_1 = \varepsilon_2 = 0.001$). Later, it will be shown that these values are optimum for a MOC solution. Next, the mass exchangeable by each of the two process lean streams is represented as an arrow versus its

respective composition scale (Fig. 4.22a). As demonstrated by Fig. 4.22b, the lean composite stream is obtained by applying superposition to the two lean arrows. Finally, the pinch diagram is constructed by combining Figs. 4.21 and 4.22b. The lean composite stream is slid vertically until it is completely above the rich composite stream.

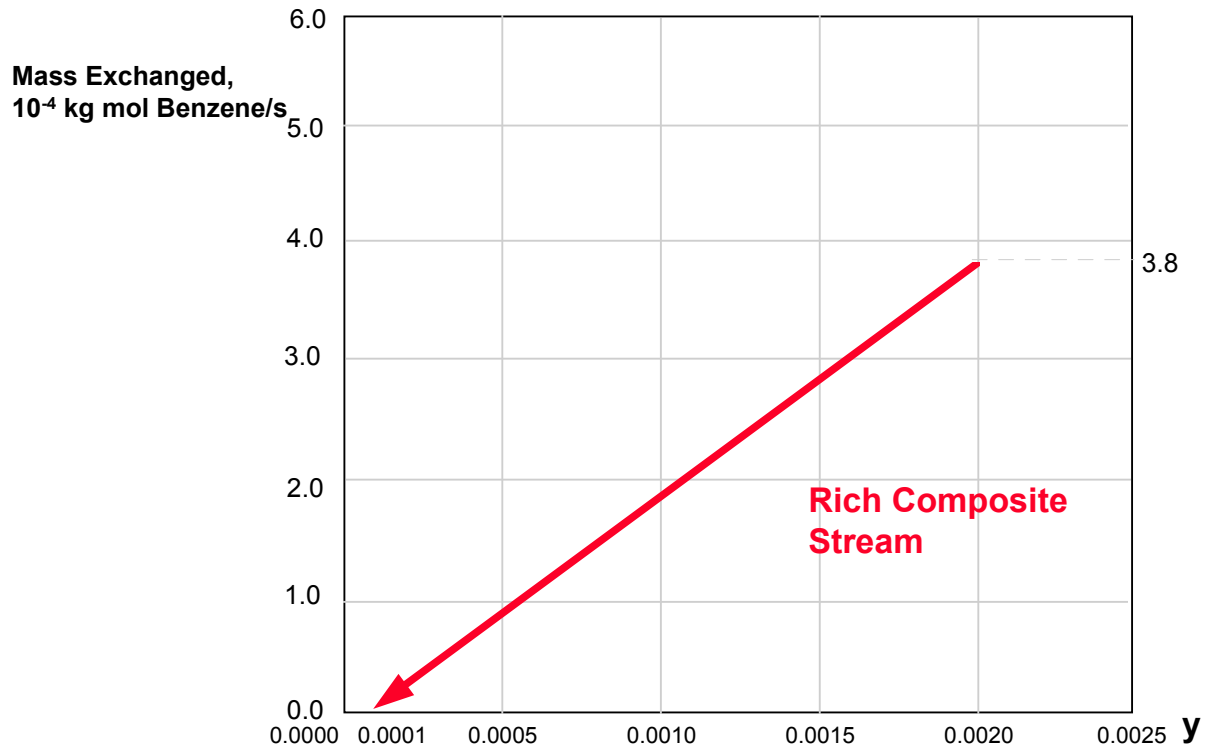


Figure 4.21. Rich composite stream for the benzene recovery example.

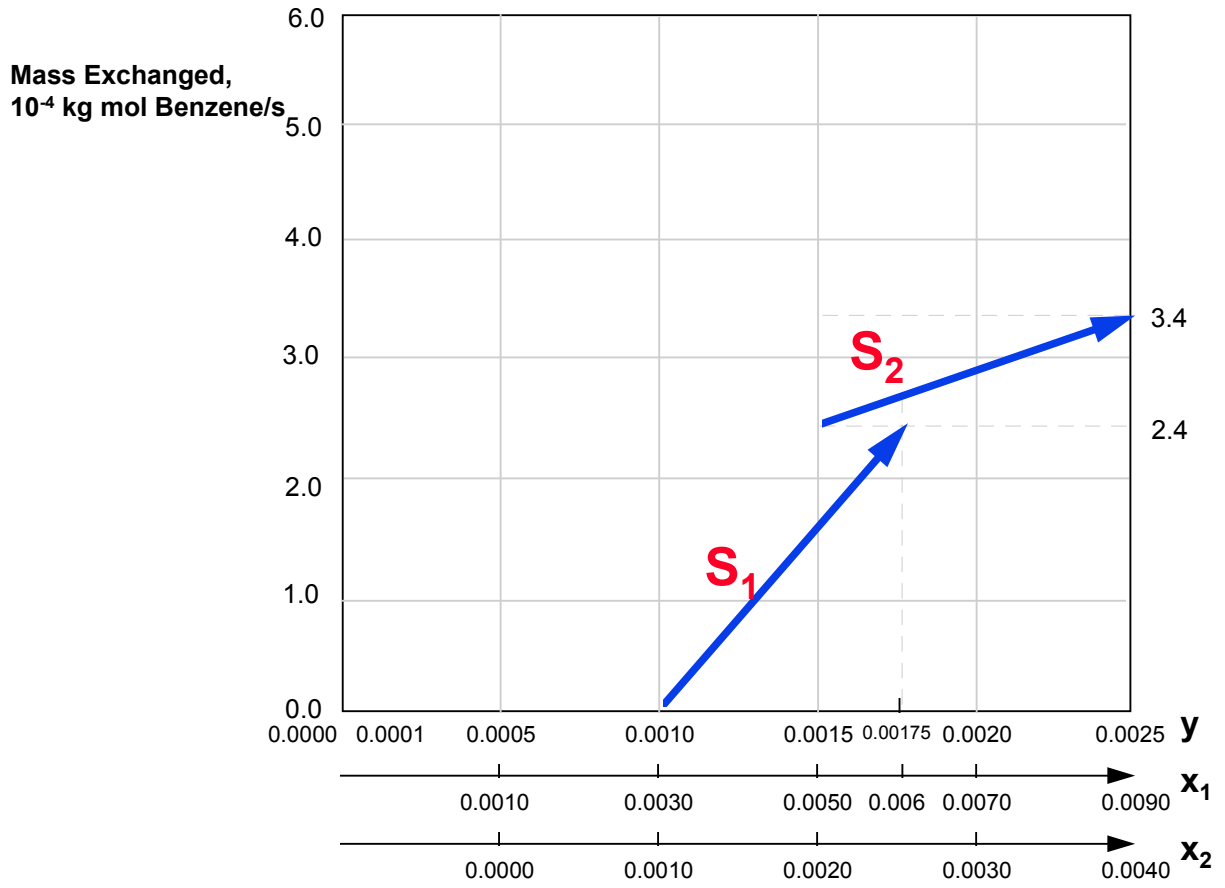


Fig. 4.22a. Representation of the two process MSAs for the benzene recovery example.

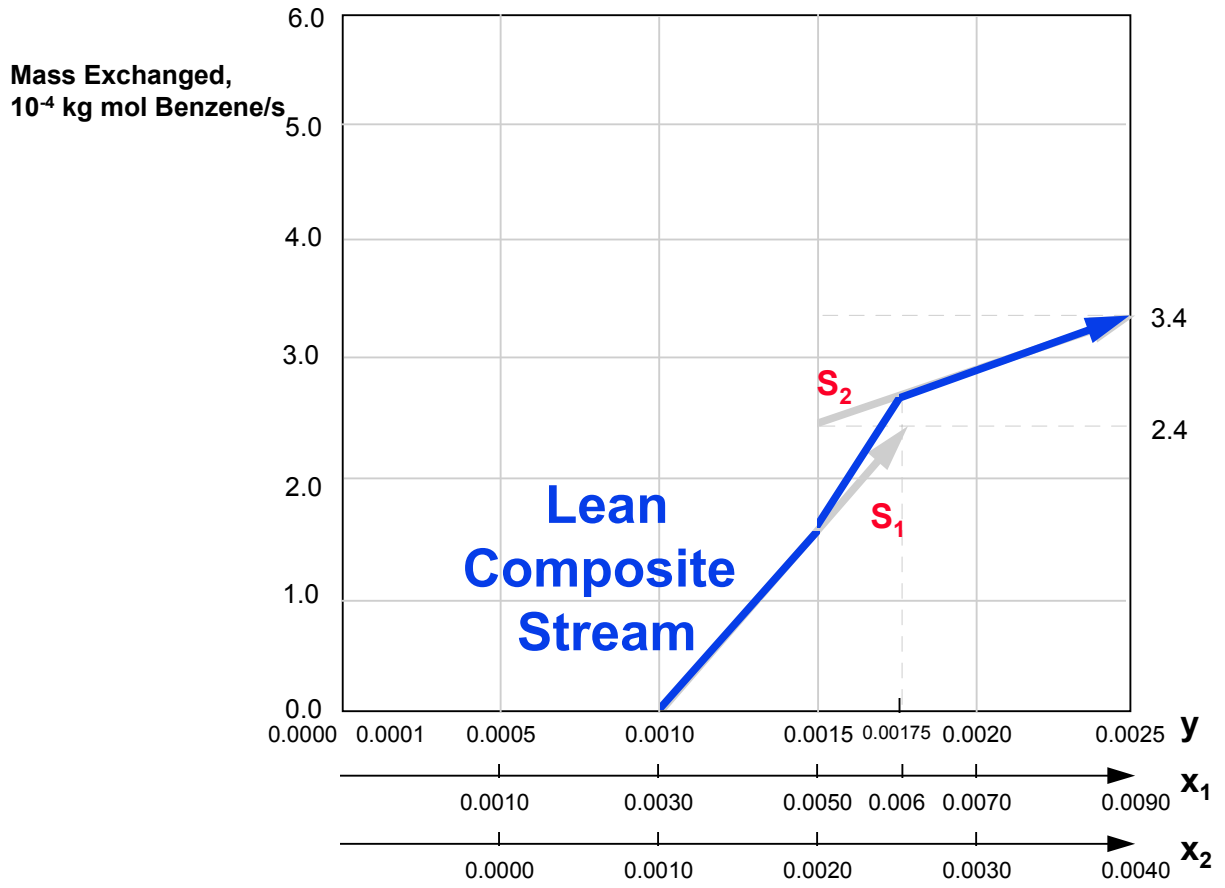


Fig. 4.22b. Construction of the lean composite stream for the two process MSA's of the benzene recovery example.

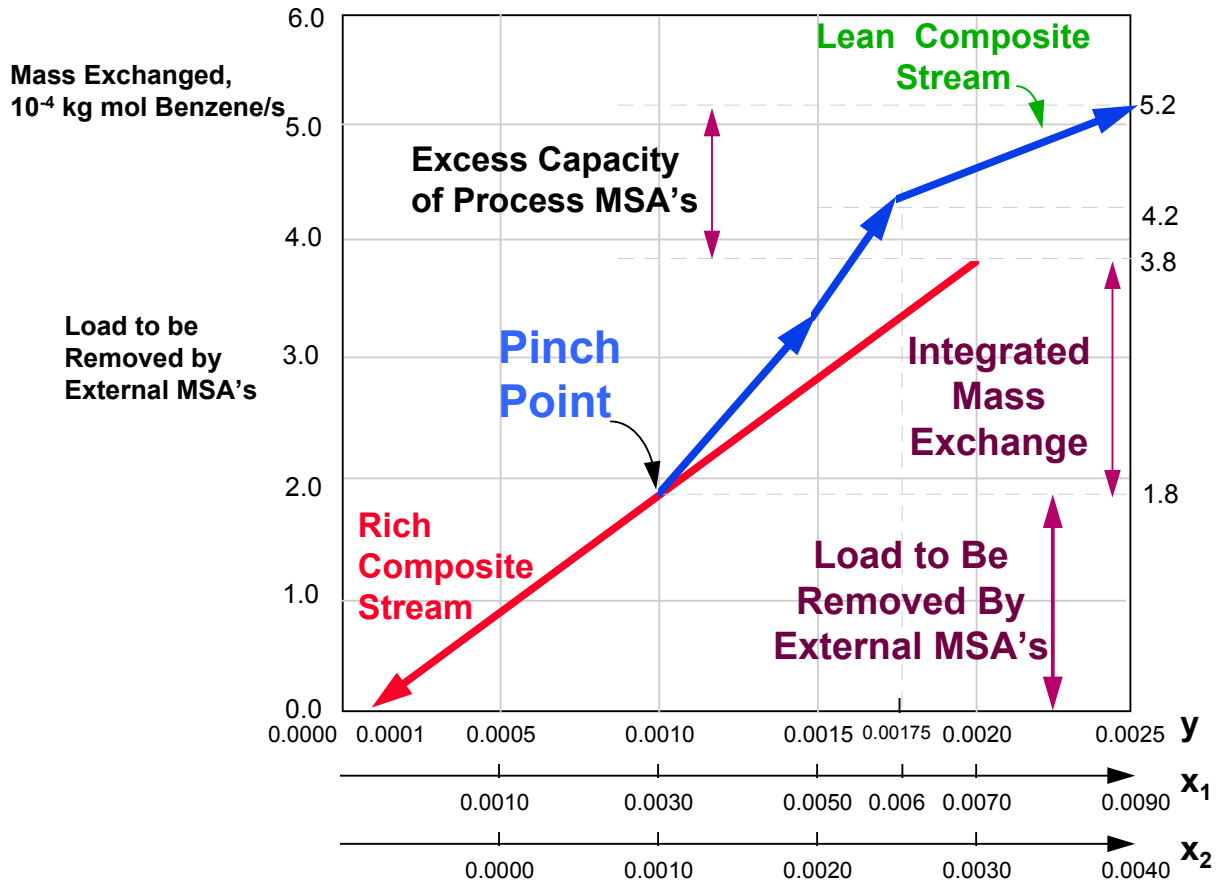


Fig. 4.23. The pinch diagram for the benzene recovery example ($\varepsilon_1 = \varepsilon_2 = 0.001$).

Interpreting Results of the Pinch Diagram

As can be seen from Fig. 4.23, the pinch is located at the corresponding mole fractions (y, x_1, x_2) = (0.0010, 0.0030, 0.0010). The excess capacity of the process MSAs is 1.4×10^{-4} kg mol benzene/s and cannot be used because of thermodynamic and practical-feasibility limitations. This excess can be eliminated by reducing the outlet compositions and/or flowrates of the process MSAs. Since the inlet composition of S_2 corresponds to a mole fraction of 0.0015 on the y scale, the waste load immediately above the pinch (from $y=0.0010$ to $y=0.0015$) cannot be removed by S_2 . Therefore, S_1 must be included in a MOC solution. Indeed, S_1 alone can be used to remove all the

waste load above the pinch (2×10^{-4} kg mol benzene/s). To reduce the fixed cost by minimizing the number of mass exchangers, it is preferable to use a single solvent above the pinch rather than two solvents. This is particularly attractive is given the availability of the mechanically-stirred additives-mixing column for absorption. Hence, the excess capacity of the process MSAs is eliminated by avoiding the use of S_2 and reducing the flowrate and/or outlet composition of S_1 . There are infinite combinations of L_1 and x_1^{out} that can be used to remove the excess capacity of S_1 according to the following material balance:

$$\text{Benzene load above the pinch to be removed by } S_1 = L_1(x_1^{out} - x_1^s), \quad (4.47a)$$

i.e.,

$$2 \times 10^{-4} = L_1(x_1^{out} - 0.003). \quad (4.47b)$$

Nonetheless, since the additives-mixing column will be used for absorption, the whole flowrate of S_1 (0.08 kg mol/s) should be fed to the column. Hence, according to Eq. (4.47b), the outlet composition of S_1 is 0.0055. The same result can be obtained graphically as shown in Fig. 4.24. It is worth recalling that the target composition of an MSA is only an upper bound on the actual value of the outlet composition. As was shown in this example, the outlet composition of an MSA is typically selected so as to optimize the cost of the system.

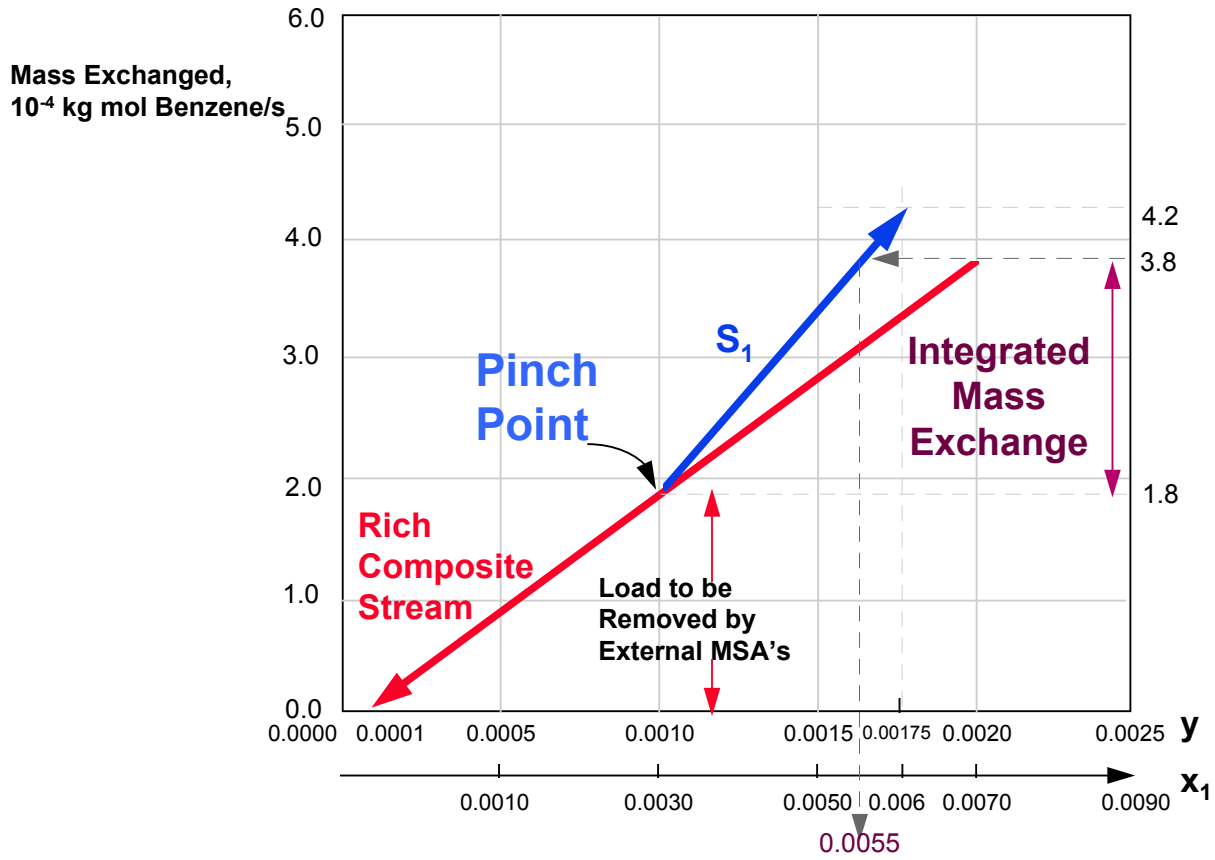


Fig. 4.24. Graphical identification of x_1^{out} .

Selection of the Optimal Value of ε_1

Since S_1 is a process MSA with almost no operating cost and since it is to be used in process equipment (the mechanically stirred column) that does not require additional capital investment for utilization as an absorption column, S_1 should be utilized to its maximum practically feasible capacity for absorbing benzene. The remaining benzene load (below the pinch) is to be removed using the external MSA. The higher the benzene load below the pinch, the higher the operating and fixed costs. Therefore, in this example it is desired to maximize the integrated mass exchanged

above the pinch. As can be seen on the pinch diagram when ε_1 increases, the x_1 axis moves to the right relative to the y axis and, consequently, the extent of integrated mass exchange decreases leading to a higher cost of external MSAs. For instance, Fig. 4.25 demonstrates the pinch diagram when ε_1 is increased to 0.002. The increase of ε_1 to 0.002 results in a load of 2.3×10^{-4} kg mol benzene/s to be removed by external MSAs (compared to 1.8×10^{-4} kg mol benzene/s for $\varepsilon_1 = 0.001$), an integrated mass exchange of 1.5×10^{-4} kg mol benzene/s (compared to 2.0×10^{-4} kg mol benzene/s for $\varepsilon_1 = 0.001$) and an excess capacity of process MSAs of 1.9×10^{-4} kg mol benzene/s (compared to 1.4×10^{-4} kg mol benzene/s for $\varepsilon_1 = 0.001$). Thus; the optimum ε_1 in this example is the smallest permissible value given in the problem statement to be 0.001.

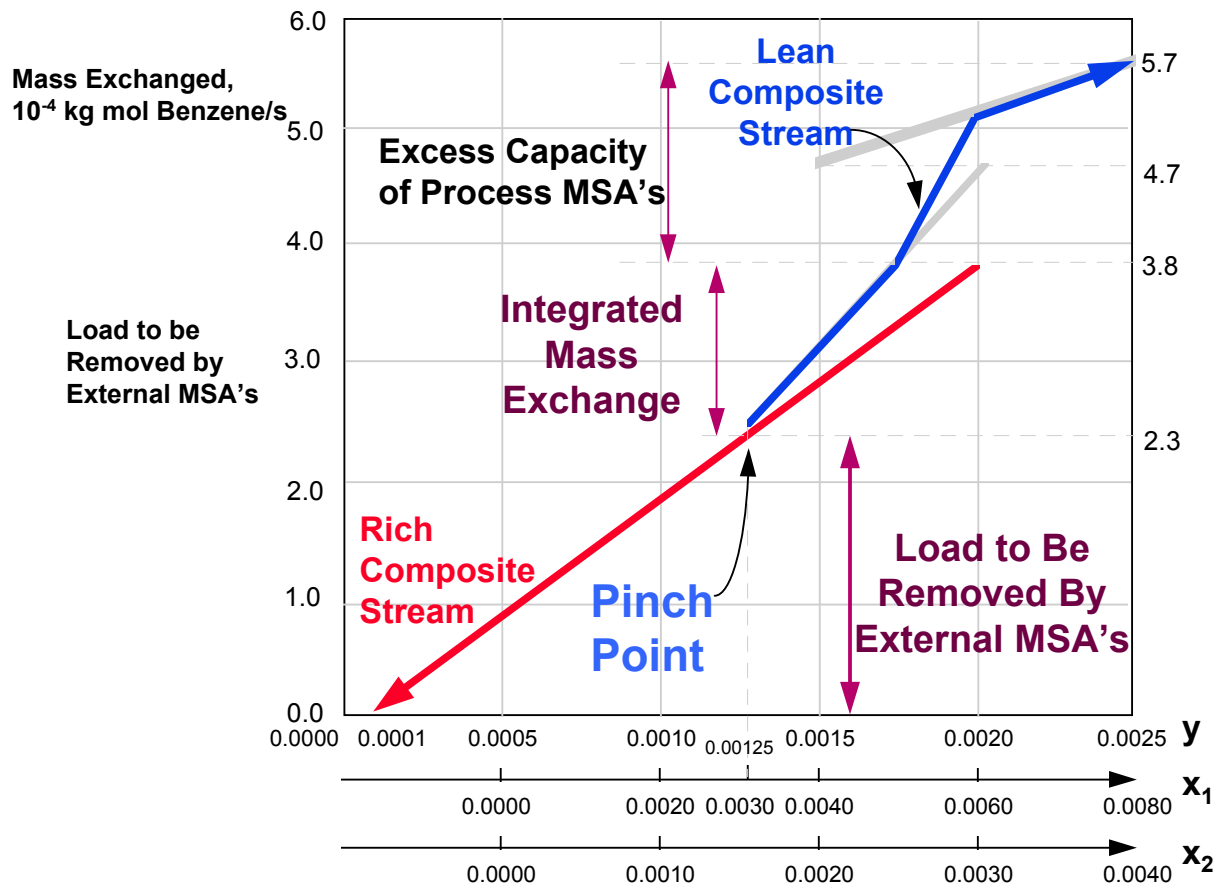


Fig. 4.25. The pinch diagram when ε_1 is increased to 0.002.

It is worth noting that there is no need to optimize over ε_2 . As previously shown, when ε_2 was set equal to its lowest permissible value (0.001), S_1 was selected as the optimal process MSA above the pinch. On the pinch diagram, as ε_2 increases, S_2 moves to the right, and the same arguments for selecting S_1 over S_2 remain valid.

Optimizing the Use of the External MSA

The pinch diagram (Fig. 4.24) demonstrates that below the pinch, the load of the waste stream has to be removed by the external MSA, S_3 . This renders the remainder of this example identical to Example 4.1. Therefore, the optimal flowrate of S_3 is 0.0234 kg mol/s and the optimal outlet composition of S_3 is 0.0085. Furthermore, the minimum total annualized cost of the benzene recovery system is \$41,560/yr (see Fig. 4.10).

Constructing the Synthesized Network

The previous analysis shows that the MEN comprises two units: one above the pinch in which R_1 is matched with S_1 , and one below the pinch in which the remainder load of R_1 is removed using S_3 . Figure 4.26 illustrates the network configuration.

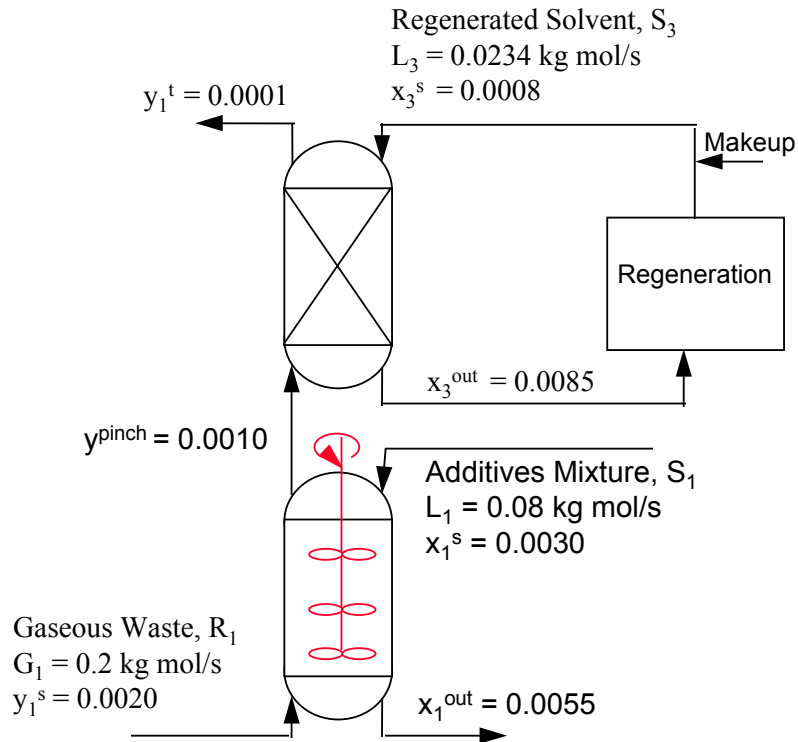


Fig. 4.26 Optimal MEN for the benzene recovery example.

4.5. SCREENING OF MULTIPLE EXTERNAL MSAs AND CONSTRUCTING THE PINCH DIAGRAM WITHOUT PROCESS MSAs

So far, construction of the mass-exchange pinch diagram started by maximizing the use of process MSAs with the consequence of minimizing the external MSAs. Then, MSAs must be screened so as to determine which one(s) should be used and the task of each MSA. Two questions arise:

- If the process has no process MSAs, how can the mass-exchange pinch analysis be carried out? Since the flowrate of each external MSA is unknown, how can the lean composite stream be constructed?
- If there are multiple external MSAs, how can they be screened?

In order to answer these questions, let us first consider the following motivating example. Suppose that it is desired to recover 10 kg/hr of hydrogen from an industrial gas stream. Two candidate adsorbents are being screened: sand whose cost is \$ 0.01 /kg of sand and activated carbon whose cost is \$1.00/kg of carbon. So, which adsorbent is cheaper? Is the cost per kg of the MSA an appropriate criterion to screen the candidate MSAs? The cost of the two adsorbents should be linked with the separation task. The following table summarizes the supply and target compositions for the two adsorbents.

Table 4.4. Data for Two Adsorbents

MSA	x^s kg H ₂ /kg MSA	x^t kg H ₂ /kg MSA
Sand	0.0	10 ⁻⁹
Activated Carbon	0.0	0.1

A material balance for the MSA around a mass exchanger can be written as follows:

$$\text{Mass removed by one kg of the MSA} = L_j (x_j^{out} - x_j^s) \quad (4.48)$$

Therefore,

$$\text{Flowrate of sand} = 10/(10^{-9} - 0.0) = 10^{10} \text{ kg sand/hr} \quad (4.49)$$

Similarly,

$$\text{Flowrate of activated carbon} = 10/(0.1 - 0.0) = 100 \text{ kg carbon/hr} \quad (4.50)$$

Therefore,

$$\text{Cost of sand} = 10^{10} \text{ kg sand/hr} * \$0.01/\text{kg sand} = \$100 \text{ million per hour !} \quad (4.51)$$

On the other hand,

$$\text{Cost of activated carbon} = 100 \text{ kg carbon/hr} * \$1.0/\text{kg carbon} = \$100/\text{hr} \quad (4.52)$$

The foregoing discussion illustrates the cost of the MSA expressed as \$/kg MSA is inappropriate in screening MSAs. Instead, the cost must be tied to the separation task. This can be achieved by identifying cost per kg removed of the targeted species. Both costs are related through material balance on the MSA. In a mass exchanger, mass of targeted species removed by unit mass of the MSA (e.g., 1.0 kg of MSA) removes is given by:

$$\text{Mass of targeted species removed by unit mass of the MSA} = x_j^t - x_j^s \quad (4.53)$$

Therefore,

$$c_j^r = \frac{c_j (\$/\text{kg MSA})}{x_j^{\text{out}} - x_j^s (\text{kg species} / \text{kg MSA})} \quad (4.54)$$

where C_j^r is removal cost of unit mass of the targeted species using the j^{th} MSA. Now that the appropriate cost criterion for the MSA has been determined, let us proceed to the screening of the MSAs. First, the rich composite line is plotted. Then, Eq. (4.20) is employed to generate the correspondence among the rich composition scale, y , and the lean composition scales for all external MSAs. Each external MSA is then represented versus its composition scale as a horizontal arrow extending between its supply and target compositions (Fig. 4.27a). Several useful insights can be gained from this diagram. Let us consider three MSAs; S_1 , S_2 and S_3 whose costs (\$/kg of recirculating MSA) are c_1 , c_2 and c_3 , respectively. These costs can be converted into \$/kg of removed solute, c_j^r , as follows:

$$c_j^r = \frac{c_j}{x_j^{\text{out}} - x_j^s} \quad \text{where } j=1, 2, 3. \quad (4.54)$$

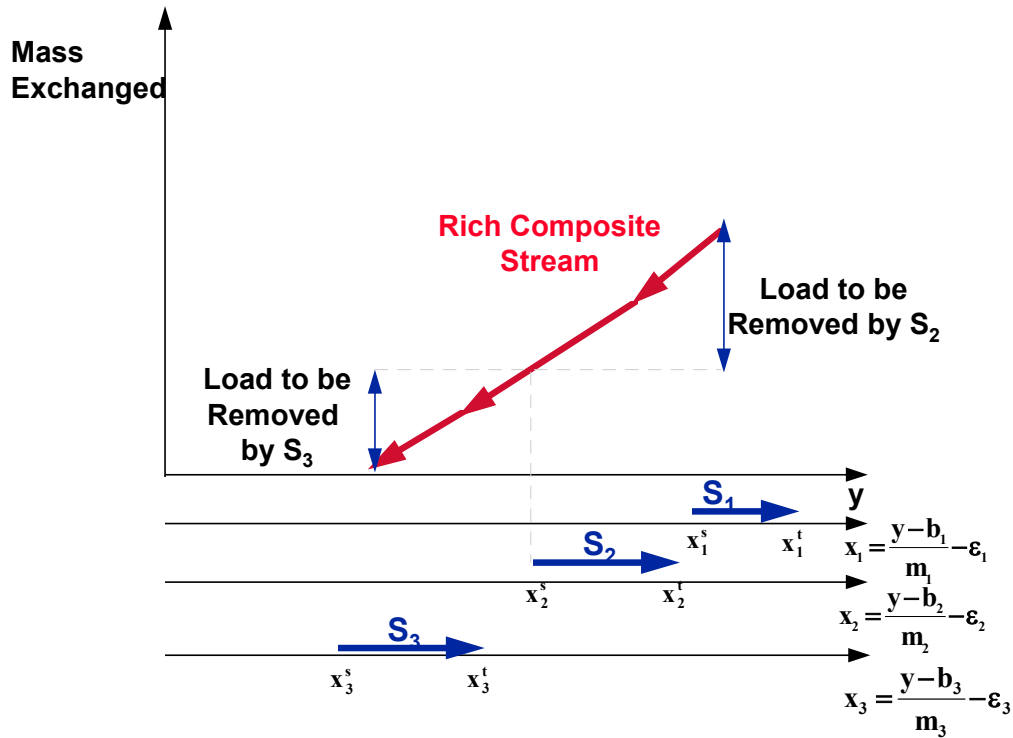


Fig. 4.27a Screening External MSA's

If arrow S_2 lies completely to the left of arrow S_1 and c_2^r is less than c_1^r , one can eliminate S_1 from the problem since it is thermodynamically and economically inferior to S_2 . On the other hand, if arrow S_3 lies completely to the left of arrow S_2 but c_3^r is greater than c_2^r , one should retain both MSAs. In order to minimize the operating cost of the network, separation should be staged to use the cheapest MSA where it is feasible. Hence, S_2 should be used to remove all the rich load to its left while the remaining rich load is removed by S_3 (Fig. 4.28a). The flowrates of S_2 and S_3 are calculated by simply dividing the rich load removed by the composition difference for the MSA. Now that the MSAs have been screened and their optimal flowrates have been determined, one can construct the pinch diagram as shown in Fig. 4.28b.

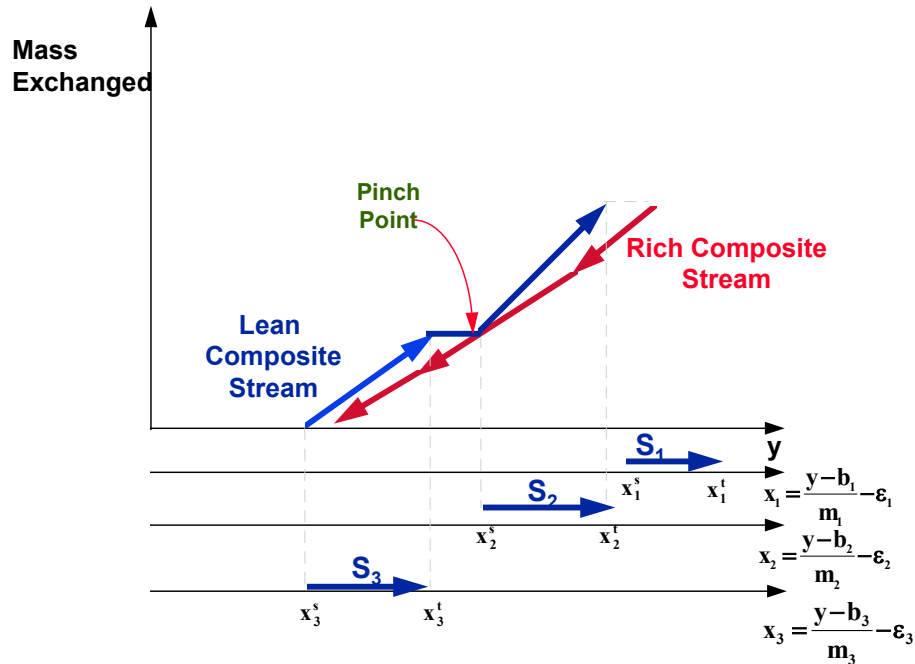


Fig. 4.28b Constructing the pinch diagram for external MSA's

4.6. Example: Wastewater Treatment

An organic pollutant is to be removed from a wastewater stream. The flowrate of the waste stream is 20 kg/s and its inlet composition of toluene is 330 ppmw. It is desired to reduced the toluene composition in water to 30 ppmw. Three external MSAs are considered: air (S_1) for stripping, activated carbon (S_2) for adsorption, and a solvent extractant (S_3). The data for the candidate MSAs are given in Table 4.5. The equilibrium data for the transfer of the pollutant from the waste stream to the j^{th} MSA is given by

$$y_l = m_j x_j \quad (4.55)$$

where y_l and x_j are the mass fractions of the toluene in the wastewater and the j^{th} MSA, respectively.

Table 4.5. Data for MSAs of Toluene Removal Example

Stream	Upper bound on flowrate L_j^C kg/s	Supply composition (ppmw) x_j^s	Target composition (ppmw) x_j^t	m_j	ϵ_j ppmw	C_j \$/kg MSA
S ₁	∞	0	9,000	0.015	5,000	3.1×10^{-3}
S ₂	∞	70	8,000	0.001	15,000	0.08
S ₃	∞	50	2,100	0.002	10,000	0.06

Use the pinch diagram to determine the minimum operating cost of the MEN.

Solution

Based on the given data and Eq. 4.54, we can calculate c_j^r to be 0.344, 10.101, and 29.268 \$/kg of pollutant removed for air, activated carbon, and extractant, respectively. Since air is the least expensive, it will be used to remove all the load to its right (0.0051 kg pollutant/s, as can be seen from Fig. 4.29a). Therefore, the flowrate of air can be calculated as

$$Flowrate\ of\ air = \frac{0.0051}{9,000 \times 10^{-6} - 0} = 0.567\ kg/s \quad (4.56)$$

Since both the activated carbon and the extractant are feasible MSAs (lying to the left of the remaining load of the rich stream), while the adsorbent has a lower c_j^r , it will be used to remove the remaining load (0.0009 kg pollutant/s, as shown by Fig. 4.29b). The flowrate of activated carbon is 0.114 kg/s. For 8000 operating hours per year, the annual operating cost of the system is \$262,000/year.

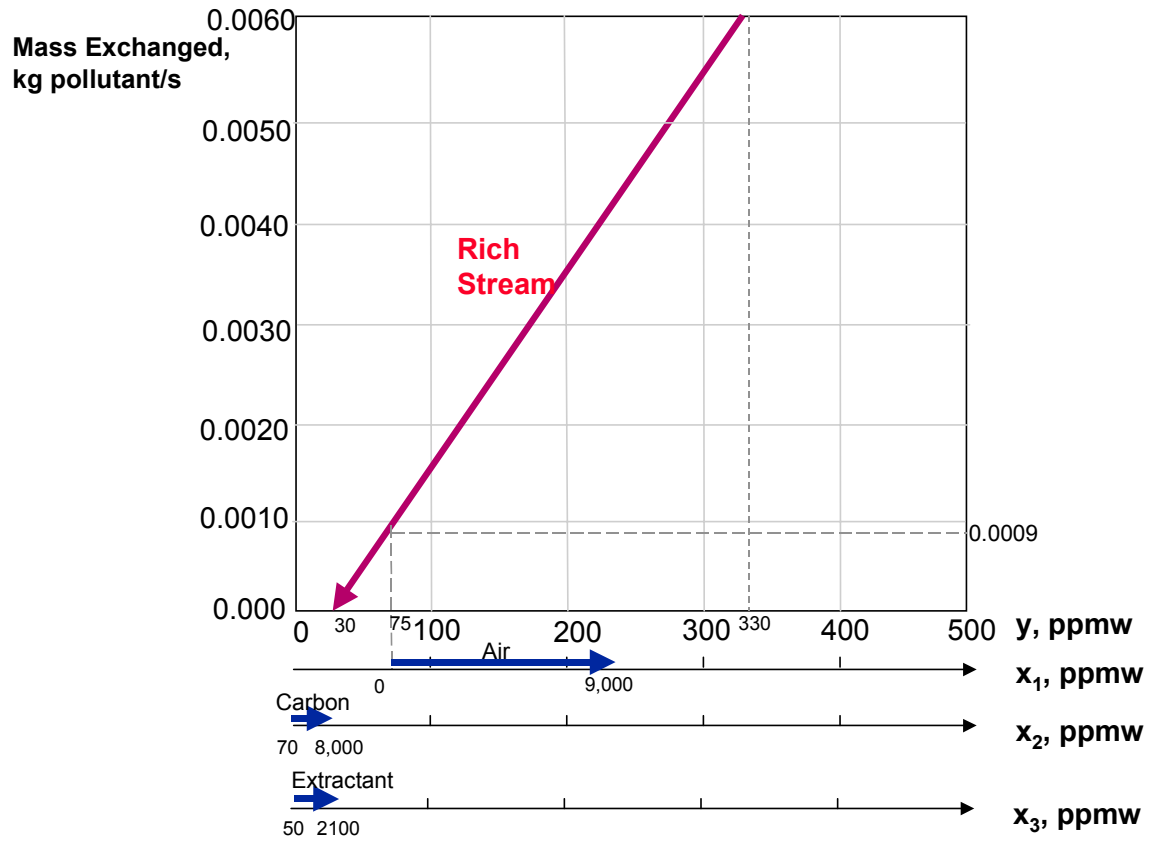


Fig. 4.29a. Screening external MSA's for the wastewater treatment example

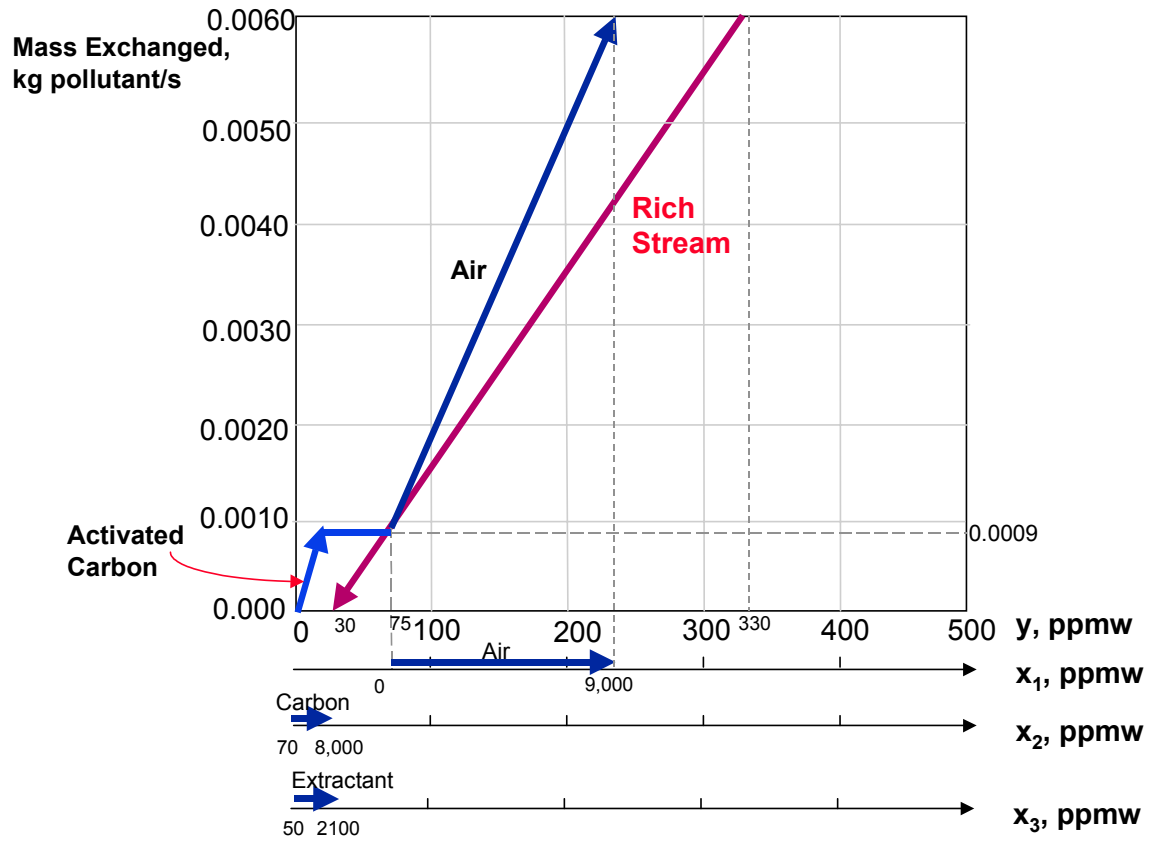


Fig. 4.29b The Pinch Diagram for the wastewater removal example.

PROBLEMS

4.1. A processing facility converts scrap tires into fuel via pyrolysis (El-Halwagi, 1997). Figure 4.30 is a simplified block flow diagram of the process. The discarded tires are fed to a high-temperature reactor where heat breaks down the hydrocarbon content of the tires into oils and gaseous fuels. The oils are further processed and separated to yield transportation fuels. The reactor off-gases are cooled to condense light oils. The condensate is decanted into two layers: organic and aqueous. The organic layer is mixed with the liquid products of the reactor. The aqueous layer is a wastewater stream whose organic content must be reduced prior to discharge. The primary pollutant in the wastewater is a heavy hydrocarbon. The data for the wastewater stream are given in Table 4.6.

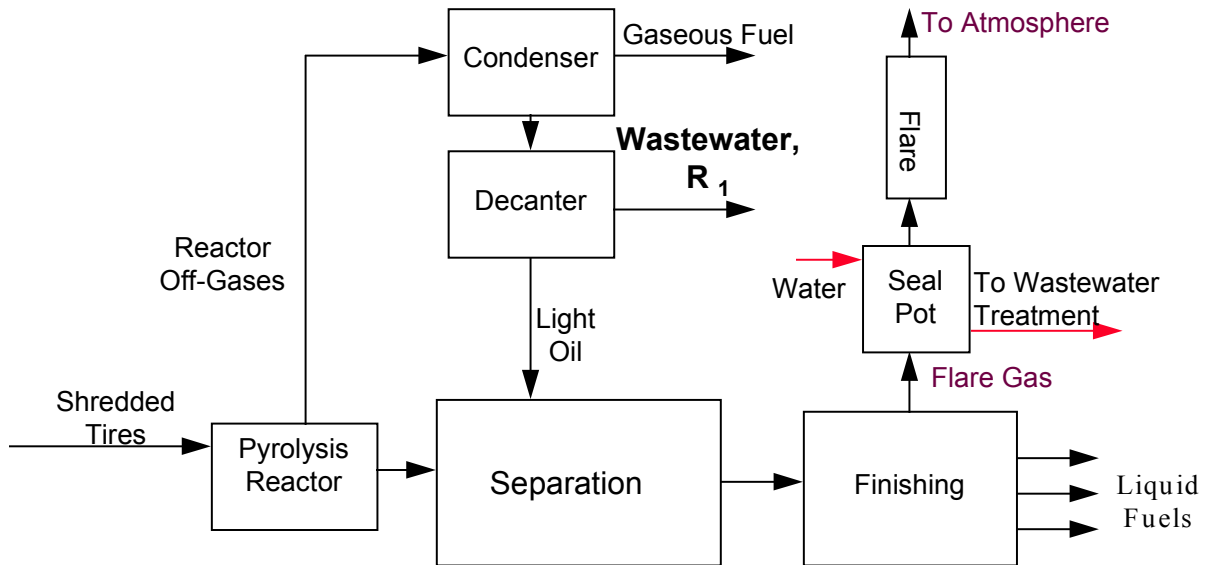


Fig. 4.30. A simplified block flow diagram of a tire-to-fuel process (El-Halwagi, 1997)

Table 4.6. Data for the Wastewater Stream of Tire Pyrolysis Plant

Stream	Description	Flowrate G_i, kg/s	Supply composition (ppmw) y_i^s	Target composition (ppmw) y_i^t
R₁	Aqueous Layer from Decanter	0.2	500	50

A process lean stream and three external MSAs are considered for removing the pollutant. The process lean stream is a flare gas (a gaseous stream fed to the flare) which can be used as a process stripping agent. To prevent the back-propagation of fire from the flare, a seal pot is used. An aqueous stream is passed through the seal pot to form a buffer zone between the fire and the source of the flare gas. Therefore, the seal pot can be used as a stripping column in which the flare gas strips the organic pollutant off the wastewater while the wastewater stream constitutes a buffer solution for preventing back-propagation of fire.

Three external MSAs are considered: a solvent extractant (S_2), an adsorbent (S_3), and a stripping agent (S_4). The data for the candidate MSAs are given in Table 4.7. The equilibrium data for the transfer of the pollutant from the waste stream to the j th MSA is given by

$$y_1 = m_j x_j \quad (4.57)$$

where y_1 and x_j are the mass fractions of the organic pollutant in the wastewater and the j^{th} MSA, respectively.

Table 4.7. Data for the MSA's of the Tire Pyrolysis Problem

Stream	Upper bound on flowrate L_j^c kg/s	Supply composition (ppmw) x_j^s	Target composition (ppmw) x_j^t	m_j	ϵ_j ppmw	C_j \$/kg MSA
S ₁	0.15	200	900	0.5	200	-
S ₂	?	300	1000	1.0	100	0.001
S ₃	?	10	200	0.8	50	0.020
S ₄	?	20	600	0.2	50	0.040

For the given data, use the pinch diagram to determine the minimum operating cost of the MEN.

4.2. If the fixed cost is disregarded in the previous problem, what is the lowest target for operating cost of the MEN? **Hint:** Set all the ϵ_j 's equal to zero.

4.3. Consider the coke-oven gas COG sweetening process shown in Fig. 4.31 (El-Halwagi and Manousiouthakis, 1989a, El-Halwagi, 1997). The basic objective of COG sweetening is the removal of acidic impurities, primarily hydrogen sulfide, from COG (a mixture of H₂, CH₄, CO, N₂, NH₃, CO₂, and H₂S). Hydrogen sulfide is an undesirable impurity, because it is corrosive and contributes to SO₂ emission when the COG is burnt. The existence of ammonia in COG and the selectivity of aqueous ammonia in absorbing H₂S suggests that aqueous ammonia is a candidate solvent (process lean stream, S₁). It is desirable that the ammonia recovered from the sour gas compensate for a large portion of the ammonia losses throughout the system and, thus, reduce 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.

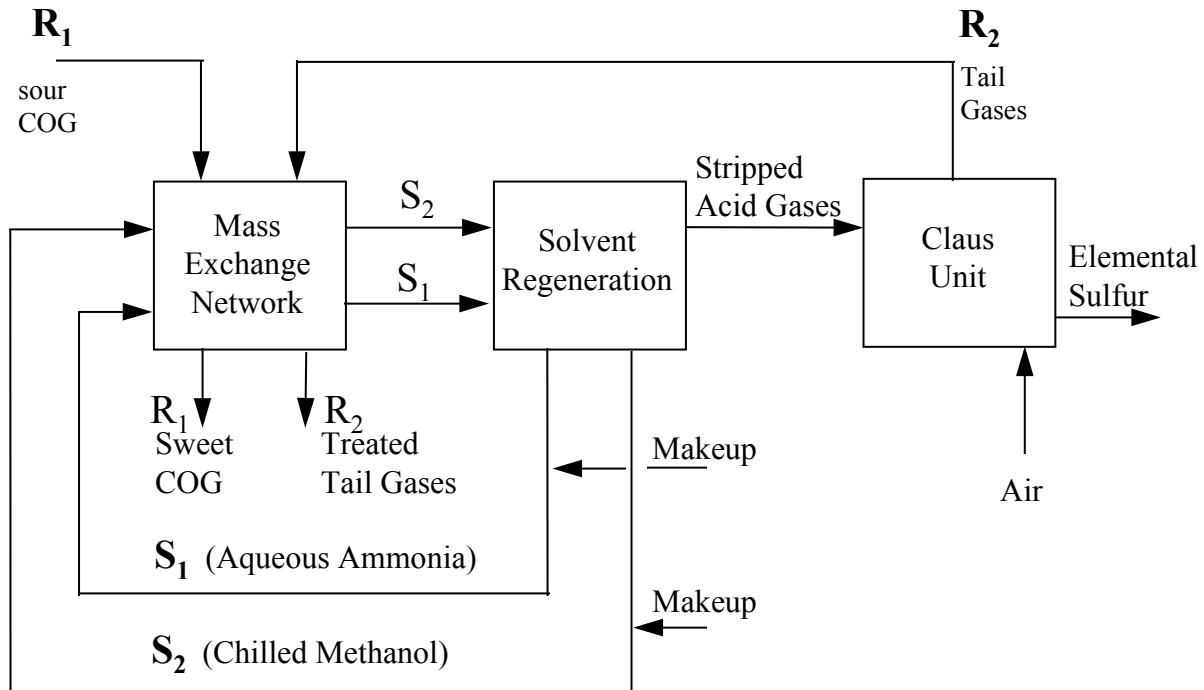


Fig. 4.31. Sweetening of COG (from El-Halwagi and Manousiouthakis, 1989).

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 MSAs 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 , should be treated for partial removal of the unconverted hydrogen sulfide. Table 4.8 summarizes the stream data.

Using the pinch diagram with $\varepsilon_1 = \varepsilon_2 = 0.0001$, find the minimum cost of MSAs required to handle the desulfurization of R_1 and R_2 . Where is the pinch located?

Table 4.8. Stream Data for the COG-Sweetening Problem

Rich stream				MSA's						
Stream	G_i (kg/s)	y_i^s	y_i^t	Stream	L_j^c kg/s	x_j^s	x_j^t	m_j	b_j	c_j \$/kg
R_1	0.90	0.0700	0.0003	S_1	2.3	0.0006	0.0310	1.45	0.000	0.00
R_2	0.10	0.0510	0.0001	S_2	?	0.0002	0.0035	0.26	0.000	0.10

4.4. Figure 4.32 is a simplified flow diagram of an oil refinery (El-Halwagi et al., 1992; El-Halwagi, 1997). The process generates two major sources of phenolic wastewater; one from the catalytic cracking unit and the other from the visbreaking system. Two technologies can be used to remove phenol from R_1 and R_2 : solvent extraction using light gas oil S_1 (a process MSA) and adsorption using activated carbon S_2 (an external MSA). Table 4.9 provides data for the streams. A minimum allowable composition difference of 0.01 can be used for the two MSAs.

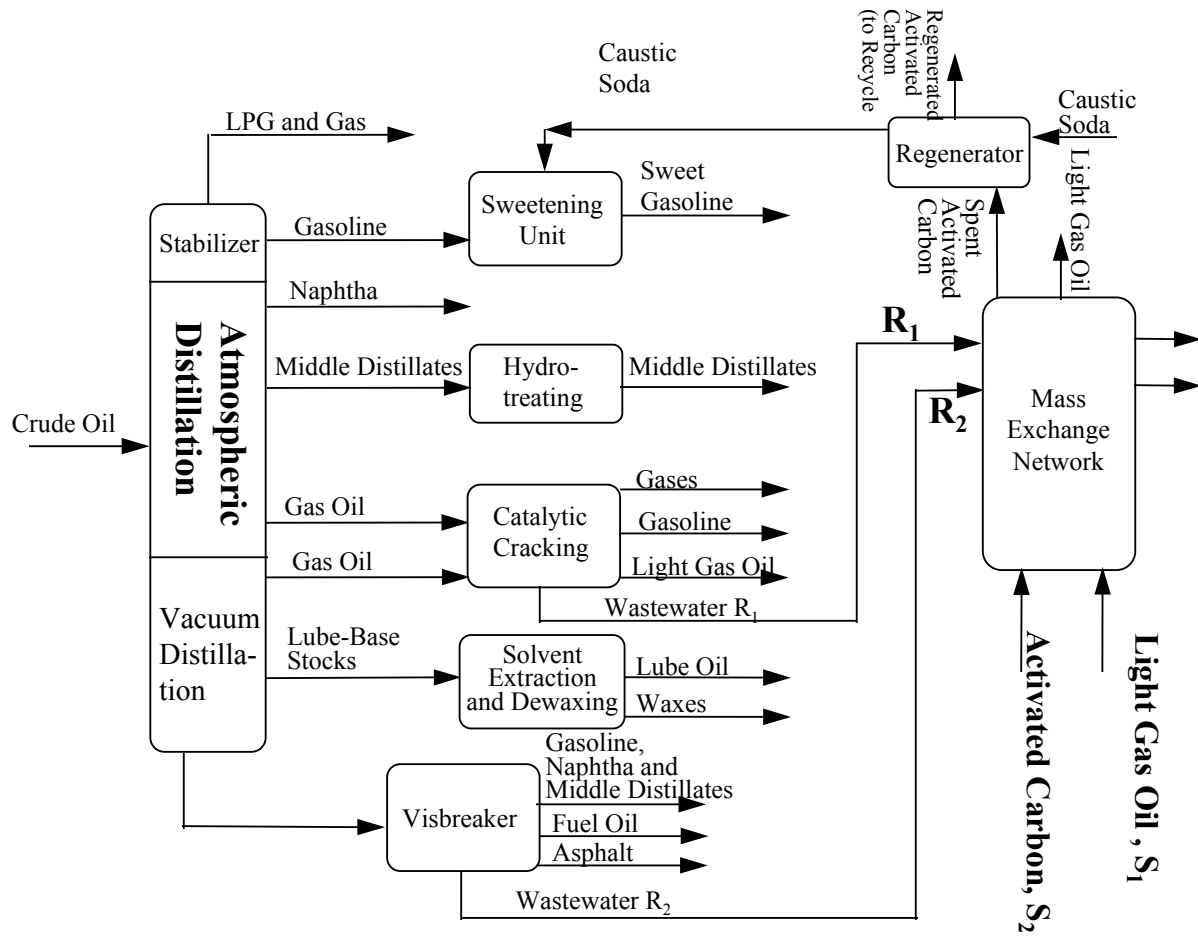


Fig. 4.32. Dephenolization of refinery wastes (from El-Halwagi et al., 1992)

Table 4.9. Stream Data for Refinery Problem

Rich stream				MSA's						
Stream	G_i (kg/s)	y_i^s	y_i^t	Stream	L_j^c (kg/s)	x_j^s	x_j^t	m_j	b_j	c_j \$/kg
R ₁	8.00	0.10	0.01	S ₁	10.00	0.01	0.02	2.00	0.00	0.00
R ₂	6.00	0.08	0.01	S ₂	?	0.00	0.11	0.02	0.00	0.08

By constructing a pinch diagram for the problem, find the minimum cost of MSAs needed to remove phenol from R₁ and R₂. How do you characterize the point at which both composite streams touch? Is it a true pinch point?

4.5. A processing facility has one rich stream, R₁, which contains a valuable byproduct and two process lean streams (S₁ and S₂), that can recover the byproduct. Three external MSAs (S₃, S₄, and S₅) are also considered for recovering the byproduct. The data for the rich stream are given in Table I. The data for the candidate MSAs are given in Table II. The equilibrium data for the transfer of the pollutant from the waste stream to the jth MSA is given by

$$y = m_j x_j$$

where y and x_j are the mass fractions of the byproduct in the rich stream and the jth MSA, respectively.

Table 4.10 Data for the Rich Stream

Stream	Description	Flowrate G_i , kg/s	Supply composition (ppmw) y_i^s	Target composition (ppmw) y_i^t
R ₁	Mixture containing byproduct	0.1	1,200	100

Table 4.11. Data for the MSA's

Stream	Upper bound	Supply	Target	m_j	ϵ_j	C_j
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	on flowrate L_j^c kg/s	composition (ppmw) x_j^s	composition (ppmw) x_j^t		ppmw	\$/kg MSA
S₁	0.1	500	700	1.0	300	-
S₂	0.3	200	350	2.0	200	-
S₃	∞	50	800	1.0	50	0.010
S₄	∞	400	1,200	3.0	100	0.002
S₅	∞	50	2,950	0.5	50	0.030

What is the minimum operating cost of the system (\$/yr)? Assume there are 8,760 operating hours per year.

4.6. Figure 4.33 shows the process flowsheet for an ethylene/ethylbenzene plant (Stanley and El-Halwagi, 1994; El-Halwagi, 1997). Gas oil is cracked with steam in a pyrolysis furnace to form ethylene, low BTU gases, hexane, heptane, and heavier hydrocarbons. The ethylene is then reacted with benzene to form ethylbenzene. Two wastewater streams are formed: R_1 which is the quench water recycle for the cooling tower and R_2 which is the wastewater from the ethylbenzene portion of the plant. The primary pollutant present in the two wastewater streams is benzene. Benzene must be removed from Stream R_1 down to a concentration of 200 ppm before R_1 can be recycled back to the cooling tower. Benzene must also be removed from stream R_2 down to a concentration of 360 ppm before R_2 can be sent to biotreatment. The data for streams R_1 and R_2 are shown in Table 4.12.

Table 4.12. Data for the Waste Streams of the Ethylbenzene Plant (Stanley and El-Halwagi, 1994)

Stream	Description	Flowrate G_i kg/s	Supply Composition (ppmw) y_i^s	Target Composition (ppmw) y_i^t
	Wastewater			

R ₁	from Settling	100	1000	200
R ₂	Wastewater from Ethylbenzene Separation	50	1,800	360

There are two process MSAs available to remove benzene from the wastewater streams. These process MSA's are hexane (S₁) and heptane (S₂). Hexane is available at a flowrate of 0.8 kg/s and supply composition of 10 ppmw while heptane is available at a flowrate of 0.3 kg/s and supply composition of 15 ppmw. The target compositions for hexane and heptane are unknown and should be determined by the engineer designing the MEN. The mass-transfer driving forces, ε_1 and ε_2 , should be at least 30,000 and 20,000 ppmw, respectively. The equilibrium data for benzene transfer from wastewater to hexane and heptane are:

$$y = 0.011x_1 \quad (4.58)$$

and

$$y = 0.008x_2, \quad (4.59)$$

where y , x_1 and x_2 are given in mass fractions.

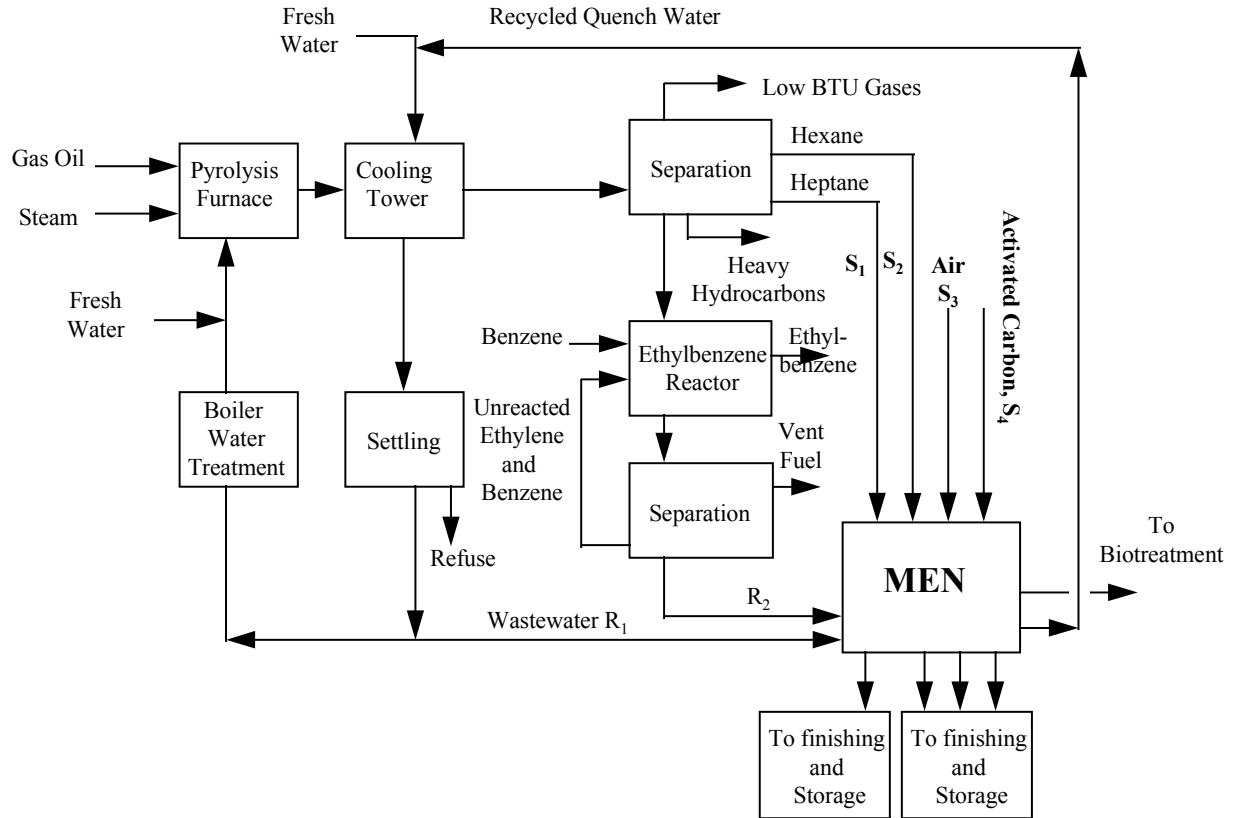


Fig. 4.33 Process Flowsheet for an Ethylene/Ethylbenzene Plant (Stanley and El-Halwagi, 1994)

Two external MSAs are considered for removing benzene; air (S_3) and activated carbon (S_4). Air is compressed to 3 atm before stripping. Following stripping, benzene is separated from air using condensation. Henry's law can be used to predict equilibrium for the stripping process. Activated carbon is continuously regenerated using steam in the ratio of 1.5 kg steam:1 kg of benzene adsorbed on activated carbon. Makeup at the rate of 1% of recirculating activated carbon is needed to compensate for losses due to regeneration and deactivation. Over the operating range, the equilibrium relation for the transfer of benzene from wastewater onto activated carbon can be described by:

$$y = 7.0 \times 10^{-4} x_4 \quad (4.60)$$

a. Using the pinch diagram determine the pinch location, minimum load of benzene to be removed by external MSAs and excess capacity of process MSAs. How do you remove this excess capacity?

b. Considering the four candidate MSA's, what is the MOC needed to remove benzene?

Table 4.13. Data for the MSAs

Stream	Upper Bound on Flowrate L_j^C kg/s	Supply Composition (mass fraction) x_j^s	Target Composition (mass fraction) x_j^t	m_j	ϵ_j mass fraction	C_j \$/kg MSA
S_1	∞	0.014	0.040	0.4	0.001	0.002
S_2	∞	0.020	0.080	1.5	0.001	0.001
S_3	∞	0.001	0.010	0.1	0.001	0.002

- Using the pinch diagram, determine which solvent(s) should be employed to remove the solvent? What is the MOC for the solvent removal task? **Hint:** Consider segregating the two waste streams and removing solvent from one of them. The annualized fixed cost of a mass exchanger, \$/yr, may be approximated by $18,000 (\text{Gas Flowrate, kg/s})^{0.65}$.
- The value of the recovered solvent is \$0.80/kg of organic solvent. What is the annual gross revenue (annual value of recovered solvent - total annualized cost of solvent recovery system)?

4.8. Consider the oil-recycling plant shown in Fig. 4.35 (El-Halwagi, 1997). In this plant, two types of waste oil are handled: gas oil and lube oil. The two streams are first deashed and demetallized. Next, atmospheric distillation is used to obtain light gases, gas oil, and a heavy product. The heavy product is distilled under vacuum to yield lube oil. Both the gas oil and the lube oil should be further processed to attain desired properties. The gas oil is steam stripped to remove light and sulfur impurities, then hydrotreated. The lube oil is dewaxed/deasphalted using solvent extraction followed by steam stripping.

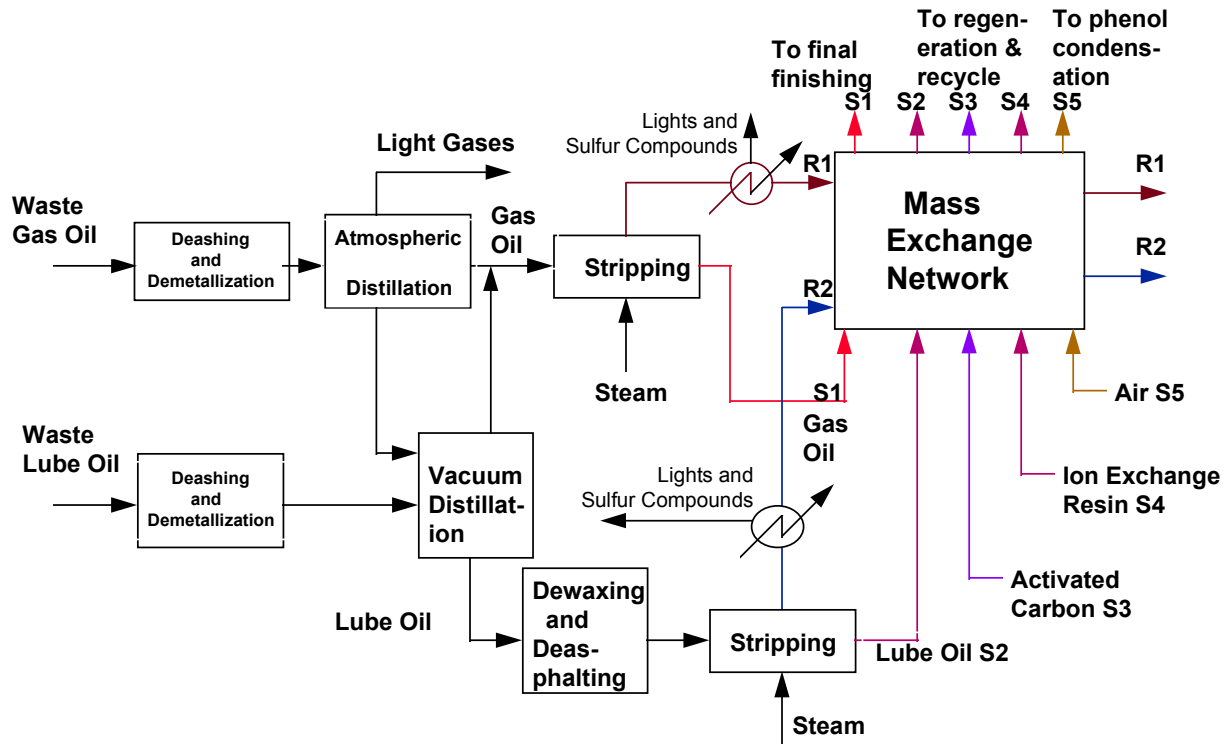


Fig. 4.35. Schematic representation of an oil recycling plant (El-Halwagi, 1997)

The process has two main sources of waste water. These are the condensate streams from the steam strippers. The principal pollutant in both wastewater streams is phenol. Phenol is of concern primarily because of its toxicity, oxygen depletion, and turbidity. In addition, phenol can cause objectionable taste and odor in fish flesh and potable water.

Several techniques can be used to separate phenol. Solvent extraction using gas oil or lube oil (process MSAs: S_1 and S_2 , respectively) is a potential option. Besides the purification of wastewater, the transfer of phenol to gas oil and lube oil is a useful process for the oils. Phenol tends to act as an oxidation inhibitor and serves to improve color stability and reduce sediment

formation. The data for the waste streams and the process MSAs are given in Tables 4.14 and 4.15, respectively.

Table 4.14. Data of waste streams for the dephenolization example (El-Halwagi, 1997)

Stream	Description	Flowrate G_i, kg/s	Supply composition y_i^s	Target composition y_i^t
R ₁	Condensate from first stripper	2	0.050	0.010
R ₂	Condensate from second stripper	1	0.030	0.006

Table 4.15. Data of process MSA's for the dephenolization example (El-Halwagi, 1997)

Stream	Description	Upper Bound on Flowrate L_j^c, kg/s	Supply Composition, x_j^s	Target Composition, x_j^t
S ₁	Gas oil	5	0.005	0.015
S ₂	lube oil	3	0.010	0.030

Three external technologies are also considered for the removal of phenol. These processes include adsorption using activated carbon, S_3 , ion exchange using a polymeric resin, S_4 , and stripping using air, S_5 . The equilibrium data for the transfer of phenol to the j^{th} lean stream is given by $y = m_j x_j$ where the values of m_j are 2.00, 1.53, 0.02, 0.09 and 0.04 for S_1 , S_2 , S_3 , S_4 and S_5 , respectively. Throughout this example, a minimum allowable composition difference, ϵ_j , of 0.001(kg phenol)/(kg MSA) will be used. The data for the three external MSAs are given in Table 4.16.

Table 4.16. Data for the External MSAs (El-Halwagi, 1997)

Stream	Upper Bound on Flowrate L_j^c kg/s	Supply Composition (mass fraction) x_j^s	Target Composition (mass fraction) x_j^t	C_j \$/kg MSA
S_3	∞	0.000	0.110	0.081
S_4	∞	0.000	0.186	0.214
S_5	∞	0.000	0.029	0.060

What is the minimum operating cost of the MEN?

SYMBOLS

b_j	intercept of equilibrium line for the j th MSA
C_j	unit cost of the j th MSA including regeneration and makeup, \$/unit flowrate of recirculating MSA
C_j^r	unit cost of the j th MSA required to remove a unit mass/mole of the key pollutant,
G_i	Flowrate of the i th waste stream
i	index for waste streams
j	index for MSA's
L_j	flowrate of the j th MSA
L_j^C	upper bound on the available flowrate of the j th MSA
m_j	slope of equilibrium line for the j th MSA
MR_i	mass/moles of pollutant lost from the i th waste stream
MS_j	mass/moles of pollutant gained by the j th MSA as defined
N_i	number of independent synthesis problems
N_S	number of MSAs
N_{SE}	number of external MSAs
N_{SP}	number of process MSAs
N_R	number of rich (waste) streams
R_i	the i th waste stream
S_j	the j th MSA
x_j	composition of key component in the j th MSA
x_j^{in}	inlet composition of key component in the j th MSA

- $x_j^{in,max}$ maximum practically-feasible inlet composition of key component in the j th MSA
- $x_j^{in,*}$ maximum thermodynamically-feasible inlet composition of key component in the j th MSA
- x_j^{out} outlet composition of key component in the j th MSA
- x_j^s supply composition of the key component in the j th MSA
- x_j^t target composition of the key component in the j th MSA
- x_j^* composition of key component in the j th MSA which is in equilibrium with y_i
- y composition scale for the key component in any waste stream
- y_i composition of key component in the i th waste stream
- y_i^s supply composition of key component in the i th waste stream
- y_i^t target composition of key component in the i th waste stream

Greek

- ε_j minimum allowable composition difference for the j th MSA

ADDITIONAL READINGS

The original MEN work was introduced by El-Halwagi and Manousiouthakis (1989). Since then, numerous papers have been published on the subject. Multicomponent MENs can also be systematically synthesized (e.g., El-Halwagi and Manousiouthakis, 1998b), Alva-Argaez et al (1999). El-Halwagi and Manousiouthakis (1990a,b) developed mathematical programming techniques to synthesize MENs as well as the regeneration systems. Genetic algorithms techniques were employed to synthesize MENs (Garrard and Fraga, 1998; Xue et al., 2000). Srinivas and El-Halwagi introduced the problem of reactive mass exchange networks (El-Halwagi and Srinivas, 1992; Srinivas and El-Halwagi, 1994a). The design of MEN-hybrid systems was addressed by El-Halwagi et al. (1992) and Hamad et al. (1996). The simultaneous design of mass- and heat-exchange networks was addressed by Srinivas and El-Halwagi, 1994b and Sebastian et al, 1996). Kiperstok and Sharratt (1995) solved the problem of synthesizing MENs with fixed-load removal. Mass exchange networks with variable supply and target compositions were tackled by (Garrison et al., 1995b). Fixed-cost targeting techniques were developed by Hallale and Fraser (Hallale and Fraser, 1997, 1999). Other classes of MENs include those providing flexible performance (Zhu and El-Halwagi, 1995). Papalexandri and Pistikopoulos, 1994), and controllable MENs (Huang and Edgar, 1995; Huang and Fan, 1995). Batch MENs have been synthesized by Foo et al. (2004). Furthermore, mass-pinch diagrams have been developed for a single lean stream for resource conservation such as minimizing water use (Wang and Smith, 1994; Dhole et al., 1996; Kuo and Smith, 1998, Mann and Liu, 1999) and managing process hydrogen (Towler, 1996).

Many industrial applications of species interception have also been published including petroleum refining (El-Halwagi and El-Halwagi, 1992; El-Halwagi et al., 1992), pulp and paper (Hamad et al., 1995, 1998; Dunn and El-Halwagi, 1993), synthetic fuels (Warren et al., 1995), petrochemicals (Stanley and El-Halwagi, 1995), and metal finishing (El-Halwagi and Manousiouthakis, 1990a). In addition, many examples illustrating the detailed application of

MEN's and mass integration to pollution prevention are published in a recent (El-Halwagi, 1997; El-Halwagi and Spriggs, 1998, Dunn and El-Halwagi, 2003).

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