Synthesis of Mass-Exchange Networks: A Mathematical Programming Approach

As has been discussed in Chapter One, mathematical programming (or optimization) is a powerful tool for process integration. For an overview of optimization and its application in pollution prevention, the reader is referred to El-Halwagi (1995). In this chapter, it will be shown how optimization techniques enable the designer to:

- Simultaneously screen all MSAs even when there are no process MSAs
- Determine the MOC solution and locate the mass-exchange pinch point
- Determine the best outlet composition for each MSA
- Construct a network of mass exchangers which has the least number of units that realize the MOC solution.

6.1 Generalization of the Composition Interval Diagram

The notion of a CID has been previously discussed in Section 5.1. This notion will now be generalized by incorporating external MSAs. In the generalized CID, $N_S + 1$ composition scales are created. First, a single composition scale, y, is established for the waste streams. Next, Eq. (3.5) is utilized to generate N_S corresponding composition scales (N_{SP} for process MSAs and N_{SE} for external MSAs). The locations corresponding to the supply and target compositions of the streams determine a sequence of composition intervals. The number of these intervals depends on the number of streams through the following inequality

$$N_{int} \leq 2(N_R + N_S) - 1. \tag{6.1}$$

The construction of the CID allows the evaluation of exchangeable loads for each stream in each composition interval. Hence, one can create a TEL for the waste streams in which the exchangeable load of the ith waste stream within the kth interval is defined as

$$W_{i,k}^R = G_i(y_{k-1} - y_k) \tag{6.2}$$

when stream i passes through interval k, and

$$W_{i,k}^R = 0 \tag{6.3}$$

when stream i does not pass through interval k. The collective load of the waste streams within interval k, W_k^R, can be computed by summing up the individual loads of the waste streams that pass through that interval, i.e.,

$$W_k^R = \sum_{i \text{ passes through interval } k} W_{i,k}^R \tag{6.4}$$

On the other hand, since the flowrate of each MSA is unknown, exact capacities of MSAs cannot be evaluated. Instead, one can create a ***TEL per unit mass of the MSAs*** for the lean streams. In this table, the exchangeable load *per unit mass of the MSA* is determined as follows:

$$w_{j,k}^S = x_{j,k-1} - x_{j,k} \tag{6.5}$$

for the jth MSA passing through interval k, and

$$w_{j,k}^S = 0 \tag{6.6}$$

when the jth MSA does not pass through the kth interval.

6.2 Problem Formulation

Section 5.3 has presented a technique for evaluating thermodynamically-feasible material balances among process streams by using the mass-exchange cascade diagram. This technique will now be generalized to include external MSAs. Once again the objective is to minimize the cost of MSAs which can remove the pollutant from the waste streams in a thermodynamically-feasible manner. Since the flowrates of the MSAs are not known, the objective function as well as the material balances around composition intervals have to be written in terms of these flowrates. The solution of the optimization program determines the optimal flowrate of each MSA. Hence, the task of identifying the MOC of the problem can be formulated through the following optimization program (El-Halwagi and Manousiouthakis, 1990a):

$$\min \sum_{j=1}^{N_S} C_j L_j \tag{P6.1}$$

subject to

$$\delta_k - \delta_{k-1} + \sum_{j \text{ passes through interval k}} L_j w^S_{j,k} = W^R_k \quad k = 1,2,\ldots,N_{int}$$

$$L_j \geq 0, \quad j = 1, 2, \ldots, N_S$$

$$L_j \leq L^c_j, \quad j = 1, 2, \ldots, N_S$$

$$\delta_0 = 0,$$

$$\delta_{N_{int}} = 0,$$

$$\delta_k \geq 0 \quad k = 1, 2, \ldots, N_{\text{int}} - 1.$$

The above program (P6.1) is a linear program that seeks to minimize the objective function of the operating cost of MSAs where C_j is the cost of the jth MSA ($/kg of recirculating MSA, including regeneration and makeup costs) and L_j is the flowrate of the jth MSA. The first set of constraints represents successive material balances around each composition interval where δ_{k-1} and δ_k are the residual masses of the key pollutant entering and leaving the kth interval. The second and third sets of constraints guarantee that the optimal flowrate of each MSA is nonnegative and is less than the total available quantity of that lean stream. The fourth and fifth constraints ensure that the overall material balance for the problem is realized. Finally, the last set of constraints enables the waste streams to pass the mass of the pollutant downwards if it does not fully exchange it with the MSAs in a given interval. This transfer of residual loads is thermodynamically feasible owing to the way in which the CID has been constructed.

The solution of program (P6.1) yields the optimal values of all the L_j's ($j = 1, 2, \ldots, N_S$) and the residual mass-exchange loads δ_k's ($k = 1, 2, \ldots, N_{\text{int}} - 1$). The location of any pinch point between two consecutive intervals, k and $k + 1$, is indicated when the residual mass-exchange load δ_k vanishes. This is a *generalization of the concept of a mass-exchange pinch point* discussed in Section 3.6. Since the plant may not involve the use of any process MSAs, external MSAs can indeed be used above the pinch to obtain an MOC solution. However, the pinch point still maintains its significance as the most thermodynamically constrained region of the network at which all mass transfer duties take place with driving forces equal to the minimum allowable composition differences.

6.3 The Dephenolization Example Revisited

The dephenolization problem was described in Section 3.2. The data for the waste and the lean streams are summarized by Tables 6.1 and 6.2.

Table 6.1
Data for Waste Streams in Dephenolization Example

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_1	Condensate from second stripper	1	0.030	0.006

The first step in determining the MOC is to construct the CID for the problem to represent the waste streams along with the process and external MSAs. The CID is shown in Fig. (6.1) for the case when the minimum allowable composition differences are 0.001. Hence, one can evaluate the exchangeable loads for the two waste streams over each composition interval. These loads are calculated through Eqs. (6.2) and (6.3). The results are illustrated by Table 6.3.

Next, using Eqs. (6.5) and (6.6), the TEL for the lean streams per unit mass of the MSA is created. These loads are depicted in Table 6.4.

We are now in a position to formulate the problem of minimizing the cost of MSAs. By adopting the linear-programming formulation (P6.1), one can write the following optimization program:

$$\min 0.081L_3 + 0.214L_4 + 0.060L_5 \tag{P6.2}$$

Table 6.2
Data for MSAs in Dephenolization Example

Stream	Description	Upper bound on flowrate L_j^c (kg/s)	Supply composition x_j^s	Target composition x_j^t	Equilibrium distribution coefficient $m_j = y/x_j$	Cost C_j ($/kg of recirculation MSA)
S_1	Gas oil	5	0.005	0.015	2.00	0.000
S_2	Lube oil	3	0.010	0.030	1.53	0.000
S_3	Activated carbon	∞	0.000	0.110	0.02	0.081
S_4	Ion-exchange resin	∞	0.000	0.186	0.09	0.214
S_5	Air	∞	0.000	0.029	0.04	0.060

Table 6.3
TEL for Waste Streams

Interval	Load of waste streams (kg phenol/s) R_1	R_2	$R_1 + R_2$
1	0.0052	–	0.0052
2	0.0308	–	0.0308
3	0.0040	–	0.0040
4	0.0264	0.0132	0.0396
5	0.0096	0.0048	0.0144
6	0.0040	0.0020	0.0060
7	–	0.0040	0.0040
8	–	–	–
9	–	–	–
10	–	–	–
11	–	–	–
12	–	–	–

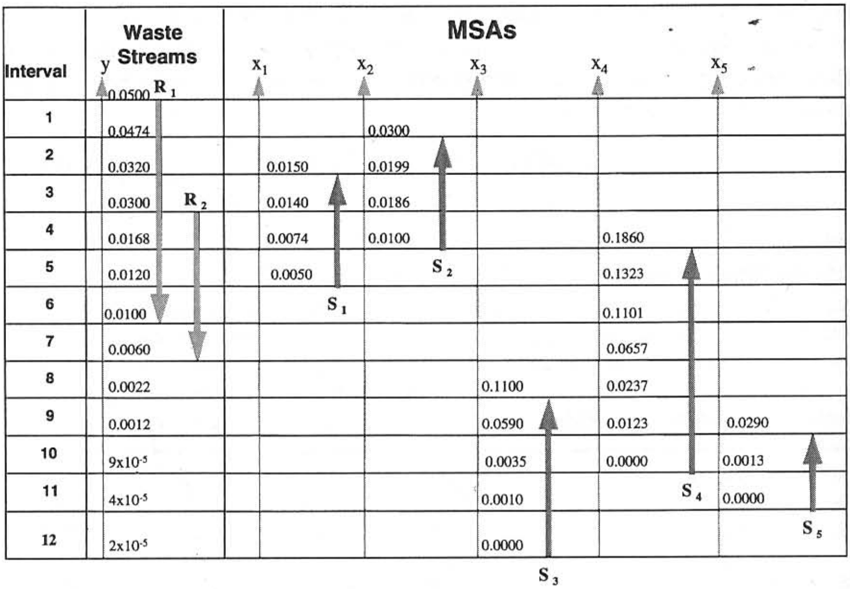

Figure 6.1 CID for dephenolization example.

Table 6.4
The TEL (kg Phenol/kg MSA) for the MSAs

	Capacity of lean streams per unit mass of MSA (kg phenol/kg MSA)				
Interval	S_1	S_2	S_3	S_4	S_5
1	–	–	–	–	–
2	–	0.0101	–	–	–
3	0.0010	0.0013	–	–	–
4	0.0066	0.0086	–	–	–
5	0.0024	–	–	0.0537	–
6	–	–	–	0.0222	–
7	–	–	–	0.0444	–
8	–	–	–	0.0420	–
9	–	–	0.0510	0.0114	–
10	–	–	0.0555	0.0123	0.0277
11	–	–	0.0025	–	0.0013
12	–	–	0.0010	–	–

subject to

$$\delta_1 = 0.0052$$

$$\delta_2 - \delta_1 + 0.0101L_2 = 0.0308$$

$$\delta_3 - \delta_2 + 0.0010L_1 + 0.0013L_2 = 0.0040$$

$$\delta_4 - \delta_3 + 0.0066L_1 + 0.0086L_2 = 0.0396$$

$$\delta_5 - \delta_4 + 0.0024L_1 + 0.0537L_4 = 0.0144$$

$$\delta_6 - \delta_5 + 0.0222L_4 = 0.0060$$

$$\delta_7 - \delta_6 + 0.0444L_4 = 0.0040$$

$$\delta_8 - \delta_7 + 0.0420L_4 = 0.0000$$

$$\delta_9 - \delta_8 + 0.0510L_3 + 0.0114L_4 = 0.0000$$

$$\delta_{10} - \delta_9 + 0.0555L_3 + 0.0123L_4 + 0.0277L_5 = 0.000$$

$$\delta_{11} - \delta_{10} + 0.0025L_3 + 0.0013L_5 = 0.0000$$

$$-\delta_{11} + 0.0010L_3 = 0.0000$$

$$\delta_k \geq 0, \quad k = 1, 2, \ldots, 11$$

$$L_j \geq 0, \quad j = 1, 2, \ldots, 5$$

$$L_1 \leq 5,$$

$$L_2 \leq 3.$$

In terms of LINGO input, program P6.2 can be written as:

```
model:
min = 0.081*L3 + 0.214*L4 + 0.060*L5;
delta1 = 0.0052;
delta2 - delta1 + 0.0101*L2 = 0.0308;
delta3 - delta2 + 0.001*L1 + 0.0013*L2 = 0.0040;
delta4 - delta3 + 0.0066*L1 + 0.0086*L2 = 0.0396;
delta5 - delta4 + 0.0024*L1 + 0.0537*L4 = 0.0144;
delta6 - delta5 + 0.0222*L4 = 0.0060;
delta7 - delta6 + 0.0444*L4 = 0.0040;
delta8 - delta7 + 0.0420*L4 = 0.0000;
delta9 - delta8 + 0.051*L3 + 0.0114*L4 = 0.000;
delta10 - delta9 + 0.0555*L3 + 0.0123*L4 + 0.0277*L5
= 0.000;
delta11 - delta10 + 0.0025*L3 + 0.0013*L5 = 0.0000;
-delta11 + 0.0010*L3 = 0.000;
delta1 >= 0.0;
delta2 >= 0.0;
delta3 >= 0.0;
delta4 >= 0.0;
delta5 >= 0.0;
delta6 >= 0.0;
delta7 >= 0.0;
delta8 >= 0.0;
delta9 >= 0.0;
delta10 >= 0.0;
delta11 >= 0.0;
L1 >= 0.0;
L2 >= 0.0;
L3 >= 0.0;
L4 >= 0.0;
L5 >= 0.0;
L1 <= 5.0;
L2 <= 3.0;
end
```

The following is the solution report generated by LINGO:

```
Optimal solution found at step:     2
Objective value:              0.9130909E-02
```

Variable	Value
L3	0.1127273
L4	0.0000000E+00
L5	0.0000000E+00
DELTA1	0.5200000E-02
DELTA2	0.1499200E-01
L2	2.080000
DELTA3	0.1128800E-01
L1	5.000000
DELTA4	0.0000000E+00
DELTA5	0.2399999E-02
DELTA6	0.8399999E-02
DELTA7	0.1240000E-01
DELTA8	0.1240000E-01
DELTA9	0.6650909E-02
DELTA10	0.3945454E-03
DELTA11	0.1127273E-03

As can be seen from the results, the solution to the linear program yields the following values for L_1, L_2, L_3, L_4, and L_5: 5.0000, 2.0800, 0.1127, 0.0000, and 0.0000, respectively. The optimum value of the objective function is $\$9.13 \times 10^{-3}$/s (approximately $\$288 \times 10^3$/yr). It is worth pointing out that the same optimum value of the objective function can also be achieved by other combinations of L_1 and L_2 along with the same value of L_3 (since both L_1 and L_2 are virtually free). The solution of P6.2 also yields a vanishing δ_4, indicating that the mass-exchange pinch is located at the line separating intervals 4 and 5. All these findings are consistent with the solutions obtained in Chapters Three and Five.

6.4 Optimization of Outlet Compositions

As has been discussed in Chapter Three, the target compositions are only upper bounds on the outlet compositions. Therefore, it may be necessary to optimize the outlet compositions.[1] A short-cut method of optimizing the outlet composition is the use of "lean substreams" (El-Halwagi, 1993; Garrison *et al.*, 1995). Consider an MSA, j, whose target composition is given by x_j^t. In order to determine the optimal outlet composition, x_j^{out}, a number, ND_j, of substreams are assumed. Each substream, d_j, *where* $d_j = 1, 2, \ldots, ND_j$, is a decomposed portion of the MSA which extends from the given x_j^s to a selected value of outlet composition,

[1] More rigorous techniques for optimizing outlet composition are described by El-Halwagi and Manousiouthakis (1990b), Garrison *et al.* (1995), and Gupta and Manousiouthakis (1995) and is beyond the scope of this book.

x^{out}_{j,d_j}, which lies between x^s_j and x^t_j. The flowrate of each substream, L_{j,d_j}, is unknown and is to be determined as part of the optimization problem. The number of substreams is dependent on the level of accuracy needed for the MEN analysis. Theoretically, an infinite number of substreams should be used to cover the whole composition span of each MSA. However, in practice few (typically less than five) substreams are needed. On the CID, the various substreams are represented against their composition scale. The formulation (P6.1) can, therefore, be revised to:

$$min \sum_{j=1}^{N_S} C_j \sum_{d_j=1}^{ND_j} L_{j,d_j} \tag{P6.3}$$

subject to

$$\delta_k - \delta_{k-1} + \sum_{\substack{j \text{ passes through} \\ \text{interval } k}} \sum_{d_j=1}^{ND_j} L_{j,d_j} w^S_{j,k} = W^R_k \quad k = 1, 2, \ldots, N_{\text{int}} \quad L_{j,d_j} \geq 0,$$

$$j = 1, 2, \ldots, N_S$$

$$\sum_{d_j=1}^{ND_j} L_{j,d_j} \leq L^C_j, \quad j = 1, 2, \ldots, N_S$$

$$\delta_0 = 0$$

$$\delta_{N_{\text{int}}} = 0$$

$$\delta_k \geq 0, \quad k = 1, 2, \ldots, N_{\text{int}} - 1.$$

The above program (P6.3) is a linear program which minimizes the operating cost of MSAs. The solution of this program determines the optimal flowrate of each substream and, consequently, the optimal outlet compositions. If more than one substream are selected, the total flowrate can be obtained by summing up the individual flowrates of the substreams while the outlet composition may be determined by averaging the outlet compositions as follows:

$$L_j = \sum_{d_j=1}^{ND_j} L_{j,d_j}, \tag{6.7}$$

$$x^{out}_j = \frac{\sum_{d_j=1}^{ND_j} L_{j,d_j} x^{out}_{j,d_j}}{L_j}. \tag{6.8}$$

In order to demonstrate this procedure, let us revisit Example 3.1 on the recovery of benzene from a gaseous emission of a polymer facility. Instead of

Table 6.5
Data for Waste Stream in Benzene Removal Example

Stream	Flowrate G_i (kg mol/s)	Supply composition (mole fraction) y_i^s	Target composition (mole fraction) y_i^t
R_1	0.2	0.0020	0.0001

determining the outlet composition of S_1 graphically, it will be determined mathematically. The stream data for the waste stream and for the lean streams are given in Tables 6.5 and 6.6.

In order to determine the optimal outlet composition of S_1, several substreams are created to span an outlet composition between x_1^s and x_1^t. Let us select six substreams with outlet compositions of 0.0060, 0.0055, 0.0050, 0.0045, 0.0040, and 0.0035. The CID for the problem is shown by Fig. 6.2.

In terms of the LINGO input, the problem can be formulated via the following linear program:

```
MODEL:
MIN = 0.05*L3;

D1 + 0.0005*L2 = 5.0E-05;
D2 - D1 + 0.0005*L11 + 0.00025*L2 = 2.5E-05;
D3 - D2 + 0.0005*L11 + 0.00025*L2 + 0.0005*L12
= 2.5E-05;
```

Table 6.6
Data for Lean Streams in Benzene Removal Example

Stream	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	m_j	C_j ($/kmol)	ε_j
S_1	0.08	0.0030	0.0060	0.25	0.00	0.0010
S_2	0.05	0.0020	0.0040[a]	0.50	0.00	0.0010
S_3	∞	0.0008	0.0085	0.10	0.05	0.0002

[a]This value is located above the inlet of R_1 on the CID and therefore must be reduced. Since R_1 has a supply composition of 0.002, the maximum practically feasible value of x_2^t is $(0.002/0.5) - 0.001 = 0.003$.

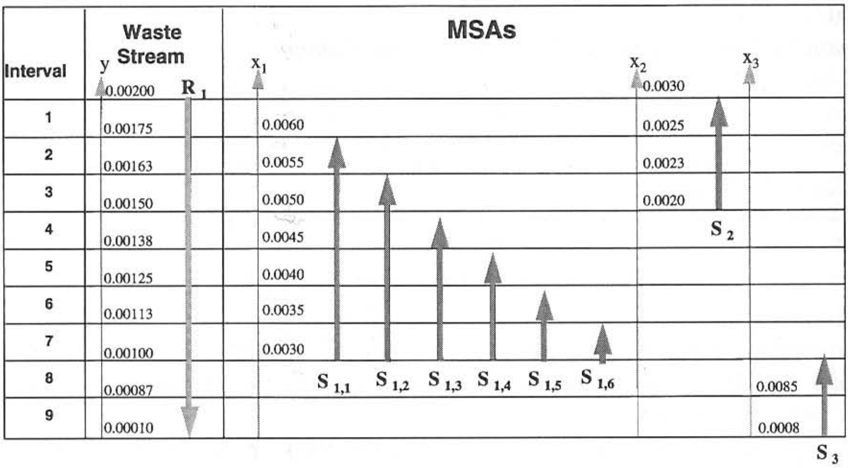

Figure 6.2 CID for benzene recovery example with lean substreams.

```
D4 - D3 + 0.0005*L11 + 0.0005*L12 + 0.0005*L13
= 2.5E-05;
D5 - D4 + 0.0005*L11 + 0.0005*L12 + 0.0005*L13
+ 0.0005*L14 = 2.5E-05;
D6 - D5 + 0.0005*L11 + 0.0005*L12 + 0.0005*L13
+ 0.0005*L14 + 0.0005*L15 = 2.5E05;
D7 - D6 + 0.0005*L11 + 0.0005*L12 + 0.0005*L13
+ 0.0005*L14 + 0.0005*L15 + 0.0005*L16 = 2.5E-05;
D8 - D7 = 2.6E-05;
- D8 + 0.0077*L3 = 0.000154;
D1 > 0.0;
D2 > 0.0;
D3 > 0.0;
D4 > 0.0;
D5 > 0.0;
D6 > 0.0;
D7 > 0.0;
D8 > 0.0;
L11 > 0.0;
L12 > 0.0;
L13 > 0.0;
L14 > 0.0;
L15 > 0.0;
L16 > 0.0;
```

```
L2 > 0.0;
L2 < 0.05;
L3 > 0.0;
L11 + L12 + L13 + L14 + L15 + L16 < 0.08;
END
```

The solution to this program yields the following results:

```
Objective value:      0.1168831E-02

           Variable          Value
             L3           0.2337662E-01
             D1           0.5000000E-04
             L2           0.0000000E+00
             D2           0.4300000E-04
             L11          0.6400000E-01
             D3           0.3600000E-04
             L12          0.0000000E+00
             D4           0.2900000E-04
             L13          0.0000000E+00
             D5           0.2200000E-04
             L14          0.0000000E+00
             D6           0.1500000E-04
             L15          0.0000000E+00
             D7           0.0000000E+00
             L16          0.1600000E-01
             D8           0.2600000E-04
```

This solution indicates that the minimum operating cost is \$33,700/yr (\$ 0.00117/s) which corresponds to an optimal flowrate of S_3 of 0.0234 kg mol/s. By applying Eqs. (6.7) and (6.8), we can determine the flowrate of S_1 to be 0.08 kg mol/s and the outlet composition to be 0.0055. The pinch location corresponds to the vanishing residual mass at the line separating intervals seven and eight ($y = 0.001$). All these results are consistent with those obtained graphically in Chapter Three. Once again, more than one solution may be obtained to give the same value of the objective function.

6.5 Stream Matching and Network Synthesis

Having identified the values of all the flowrates of lean streams as well as the pinch location, we can now minimize the number of mass exchangers for a MOC solution. As has been previously mentioned, when a pinch point exists, the synthesis problem can be decomposed into two subnetworks, one above the pinch and one below the pinch. The subnetworks will be denoted by SN_m, where $m = 1,2$. It is, therefore, useful to define the following subsets:

$$R_m = \{i \mid i \in R, \text{stream } i \text{ exists in } SN_m\} \quad (6.9)$$

$$S_m = \{j \mid j \in S, \text{stream } j \text{ exists in } SN_m\} \quad (6.10)$$

$$R_{m,k} = \{i \mid i \in R_m, \text{ stream } i \text{ exists in interval } \bar{k} \le k;\ \bar{k},\ k \in SN_m\} \quad (6.11)$$

$$S_{m,k} = \{j \mid j \in 0S_m, \text{ stream } j \text{ exists in interval } k \in SN_m\}. \quad (6.12)$$

For a rich stream, i,

$$\delta_{i,k} - \delta_{i,k-1} + \sum_{j \in S_{m,k}} W_{i,j,k} = W^R_{i,k}.$$

Within any subnetwork, the mass exchanged between any two streams is bounded by the smaller of the two loads. Therefore, the upper bound on the exchangeable mass between streams i and j in SN_m is given by

$$U_{i,j,m} = \min\left\{\sum_{k \in SN_m} W^R_{i,k}, \sum_{k \in SN_m} W^S_{j,k}\right\}. \quad (6.13)$$

Now, we define the binary variable $E_{i,j,m}$, which takes the values of 0 when there is no match between streams i and j in SN_m, and takes the value of 1 when there exists a match between streams i and j (and hence an exchanger) in SN_m. Based on Eq. (6.13), one can write

$$\sum_{k \in SN_m} W_{i,j,k} - U_{i,j,m} \le 0 \quad i \in R_m,\ j \in S_m,\ m = 1, 2, \quad (6.14)$$

where $W_{i,j,k}$ denotes the mass exchanged between the ith rich stream and the jth lean stream in the kth interval. Therefore, the problem of minimizing the number of mass exchangers can be formulated as a mixed integer linear program "MILP" (El-Halwagi and Manousiouthakis, 1990a):

$$minimize \sum_{m=1,2} \sum_{i \in R_m} \sum_{j \in S_m} E_{i,j,m}, \quad (P6.4)$$

subject to the following:

Material balance for each rich stream around composition intervals:

$$\delta_{i,k} - \delta_{i,k-1} + \sum_{j \in S_{m,k}} W_{i,j,k} = W^R_{i,k} \quad i \in R_{m,k},\ k \in SN_m,\ m = 1, 2$$

Material balance for each lean stream around composition intervals:

$$\sum_{i \in R_{m,k}} W_{i,j,k} = W^S_{j,k} \quad j \in S_{m,k},\ k \in SN_m,\ m = 1, 2$$

Matching of loads:

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

Non-negative residuals

$$\delta_{i,k} \geq 0 \quad i \in R_{m,k},\ k \in SN_m,\ m = 1, 2$$

Non-negative loads:

$$W_{i,j,k} \geq 0 \quad i \in R_{m,k}, j \in S_{m,k}, k \in SN_m,\ m = 1, 2$$

Binary integer variables for matching streams:

$$E_{i,j,m} = 0/1 \quad i \in R_m, j \in S_m,\ m = 1, 2$$

The above program is an MILP that can be solved (e.g., using the computer code LINGO) to provide information on the stream matches and exchangeable loads. It is interesting to note that the solution of program (P6.4) may not be unique. It is possible to generate all integer solutions to P6.4 by adding constraints that exclude previously obtained solutions from further consideration. For example, any previous solution can be eliminated by requiring that the sum of $E_{i,j,m}$ that were nonzero in that solution be less than the minimum number of exchangers. It is also worth mentioning that if the costs of the various exchangers are significantly different, the objective function can be modified by multiplying each integer variable by a weighing factor that reflects the relative cost of each unit.

6.6 Network Synthesis for Dephenolization Example

Let us revisit the dephenolization problem described in Sections 3.2 and 6.3. The objective is to synthesize a MOC-MEN with the least number of units. First, CID (Fig. 6.3) and the tables of exchangeable loads "TEL" (Tables 6.7 and 6.8) are developed based on the MOC solution identified in Sections 3.2 and 6.3. Since neither S_4 nor S_5 were selected as part of the MOC solution, there is no need to include them. Furthermore, since the optimal flowrates of S_1, S_2 and S_3 have been determined, the TEL for the MSAs can now be developed with the total loads of MSAs and not per kg of each MSA.

Since the pinch decomposes the problem into two subnetworks; it is useful to calculate the exchangeable load of each stream above and below the pinch. These values are presented in Tables 6.9 and 6.10.

We can now formulate the synthesis task as an MILP whose objective is to minimize the number of exchangers. Above the pinch (subnetwork $m = 1$),

Table 6.7
TEL for Waste Streams in Dephenolization Example

	Interval	Load of waste streams (kg phenol/s)	
		R_1	R_2
	1	0.0052	–
	2	0.0308	–
	3	0.0040	–
	4	0.0264	0.0132
Pinch			
	5	0.0096	0.0048
	6	0.0040	0.0020
	7	–	0.0040
	8	–	–
	9	–	–

there are four possible matches: R_1-S_1, R_1-S_2, R_2-S_1 and R_2-S_2. Hence, we need to define four binary variables ($E_{1,1,1}$, $E_{1,2,1}$, $E_{2,1,1}$, and $E_{2,2,1}$). Similarly, below the pinch (subnetwork $m = 2$) we have to define four binary variables ($E_{1,1,2} + E_{1,3,2} + E_{2,1,2} + E_{2,3,2}$) to represent potential matches between R_1-S_1,

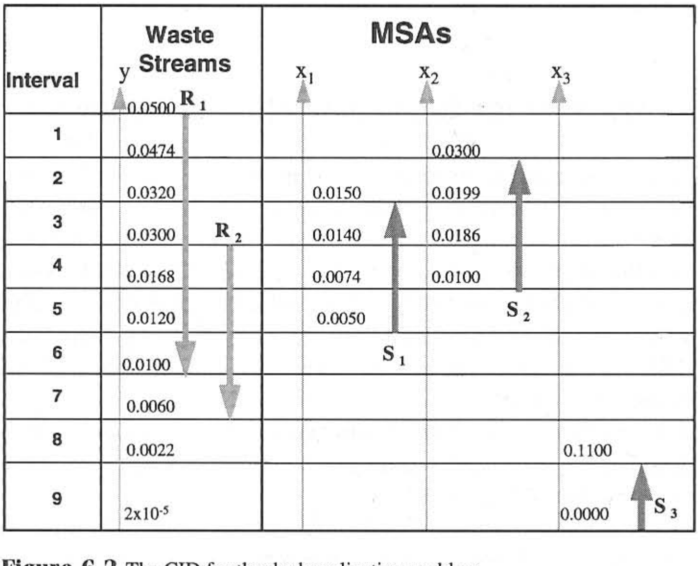

Figure 6.3 The CID for the dephenolization problem.

Table 6.8
TEL for MSAs in Dephenolization Example

	Interval	Load of MSAs (kg phenol/s)		
		S_1	S_2	S_3
	1	–	–	–
	2	–	0.0210	–
	3	0.0050	0.0027	–
	4	0.0330	0.0179	–
Pinch				
	5	0.0120	–	–
	6	–	–	–
	7	–	–	–
	8	–	–	–
	9	–	–	0.0124

Table 6.9
Exchangeable Loads Above the Pinch

Stream	Load (kg Phenol/s)
R_1	0.0664
R_2	0.0132
S_1	0.0380
S_2	0.0416
S_3	0.0000

Table 6.10
Exchangeable Loads Below the Pinch

Stream	Load (kg Phenol/s)
R_1	0.0136
R_2	0.0108
S_1	0.0120
S_2	0.0000
S_3	0.0124

R_1-S_3, R_2-S_1 and R_2-S_3. Therefore, the objective function is described by

$$\textit{Minimize} \quad E_{1,1,1} + E_{1,2,1} + E_{2,1,1} + E_{2,2,1} + E_{1,1,2} + E_{1,3,2} + E_{2,1,2} + E_{2,3,2}$$

subject to the following constraints:

Material balances for R_1 around composition intervals:

$$\delta_{1,1} = 0.0052$$
$$\delta_{1,2} - \delta_{1,1} + W_{1,2,2} = 0.0308$$
$$\delta_{1,3} - \delta_{1,2} + W_{1,1,3} + W_{1,2,3} = 0.0040$$
$$\delta_{1,4} - \delta_{1,3} + W_{1,1,4} + W_{1,2,4} = 0.0264$$
$$\delta_{1,5} - \delta_{1,4} + W_{1,1,5} = 0.0096$$
$$\delta_{1,6} - \delta_{1,5} = 0.0040$$
$$\delta_{1,7} - \delta_{1,6} = 0.0000$$
$$\delta_{1,8} - \delta_{1,7} = 0.0000$$
$$-\delta_{1,8} + W_{1,3,9} = 0.0000$$

Material balances for R_2 around composition intervals:

$$\delta_{2,4} + W_{2,1,4} + W_{2,2,4} = 0.0132$$
$$\delta_{2,5} - \delta_{2,4} + W_{2,1,5} = 0.0048$$
$$\delta_{2,6} - \delta_{2,5} = 0.0020$$
$$\delta_{2,7} - \delta_{2,6} = 0.0040$$
$$\delta_{2,8} - \delta_{2,7} = 0.0000$$
$$-\delta_{2,8} + W_{2,3,9} = 0.0000$$

Material balances for S_1 around composition intervals:

$$W_{1,1,3} = 0.0050$$
$$W_{1,1,4} + W_{2,1,4} = 0.0330$$
$$W_{1,1,5} + W_{2,1,5} = 0.0120$$

Material balances for S_2 around composition intervals:

$$W_{1,2,2} = 0.0210$$
$$W_{1,2,3} = 0.0027$$
$$W_{1,2,4} + W_{2,2,4} = 0.0179$$

Material balances for S_3 around the ninth interval:

$$W_{1,3,9} + W_{2,3,9} = 0.0124$$

Matching of loads:

$$W_{1,1,3} + W_{1,1,4} \leq 0.0380E_{1,1,1}$$

$$W_{1,2,2} + W_{1,2,3} + W_{1,2,4} \leq 0.0416E_{1,2,1}$$

$$W_{2,1,4} \leq 0.0132E_{2,1,1}$$

$$W_{2,2,4} \leq 0.0132E_{2,2,1}$$

$$W_{1,1,5} \leq 0.0120E_{1,1,2}$$

$$W_{2,1,5} \leq 0.0108E_{2,1,2}$$

$$W_{1,3,9} \leq 0.0124E_{1,3,2}$$

$$W_{2,3,9} \leq 0.0108E_{2,3,2}$$

with the non-negativity and integer constraints.

In terms of LINGO input, the above program can be written as follows:

```
MODEL:
MIN = E111 + E121 + E211 + E221 + E112 + E132 + E212
  + E232;

D11 = 0.0052;
D12 - D11 + W122 = 0.0308;
D13 - D12 + W113 + W123 = 0.0040;
D14 - D13 + W114 + W124 = 0.0264;
D15 - D14 + W115 = 0.0096;
D16 - D15 = 0.0040;
D17 - D16 = 0.0000;
D18 - D17 = 0.0000;
  - D18 + W139 = 0.0000;
D24 - W214 + W224 = 0.0132;
D25 - D24 + W215 = 0.0048;
D26 - D25 = 0.0020;
D27 - D26 = 0.0040;
D28 - D27 = 0.0000;
  - D28 + W239 = 0.0000;
W113 = 0.0050;
W114 + W214 = 0.0330;
W115 + W215 = 0.0120;
W122 = 0.0210;
```

```
W123 = 0.0027;
W124 + W224 = 0.0179;
W139 + W239 = 0.0124;
W113 + W114 <= 0.038*E111;
W122 + W123 + W124 <= 0.0416*E121;
W214 <= 0.0132*E211;
W224 <= 0.0132*E221;
W115 <= 0.012*E112;
W215 <= 0.0108*E212;
W139 <= 0.0124*E132;
W239 <= 0.0108*E232;
D11 >= 0.0;
D12 >= 0.0;
D13 >= 0.0;
D14 >= 0.0;
D15 >= 0.0;
D16 >= 0.0;
D17 >= 0.0;
D18 >= 0.0;
D24 >= 0.0;
D25 >= 0.0;
D26 >= 0.0;
D27 >= 0.0;
D28 >= 0.0;
W122 >= 0.0;
W113 >= 0.0;
W123 >= 0.0;
W124 >= 0.0;
W139 >= 0.0;
W214 >= 0.0;
W224 >= 0.0;
W215 >= 0.0;
W239 >= 0.0;
@BIN(E111);
@BIN(E121);
@BIN(E211);
@BIN(E221);
@BIN(E112);
@BIN(E132);
@BIN(E212);
@BIN(E232);
END
```

This MILP can be solved using LINGO to yield the following results:

```
Optimal solution found at step:   13
Objective value:               7.000000
Branch count:                     0
```

Variable	Value
E111	1.000000
E121	1.000000
E211	0.000000
E221	1.000000
E112	1.000000
E132	1.000000
E212	1.000000
E232	1.000000
D11	0.5200000E-02
D12	0.1500000E-01
W122	0.2100000E-01
D13	0.1130000E-01
W113	0.5000000E-02
W123	0.2700000E-02
D14	0.0000000E+00
W114	0.3300000E-01
W124	0.4699999E-02
D15	0.2400000E-02
W115	0.7200001E-02
D16	0.6400000E-02
D17	0.6400000E-02
D18	0.6400000E-02
W139	0.6400000E-02
D24	0.0000000E+00
W214	0.00000000E+00
W224	0.1320000E-01
D25	0.0000000E+00
W215	0.4800000E-02
D26	0.2000000E-02
D27	0.6000000E-02
D28	0.6000000E-02
W239	0.6000000E-02

These results indicate that the solution features seven units that represent matches between R_1-S_1, R_1-S_2, and R_2-S_2 above the pinch and R_1-S_1, R_1-S_3, R_2-S_1 and R_2-S_3 below the pinch. The load for each exchanger can be evaluated by simply adding up the exchangeable loads within the same subnetwork. For

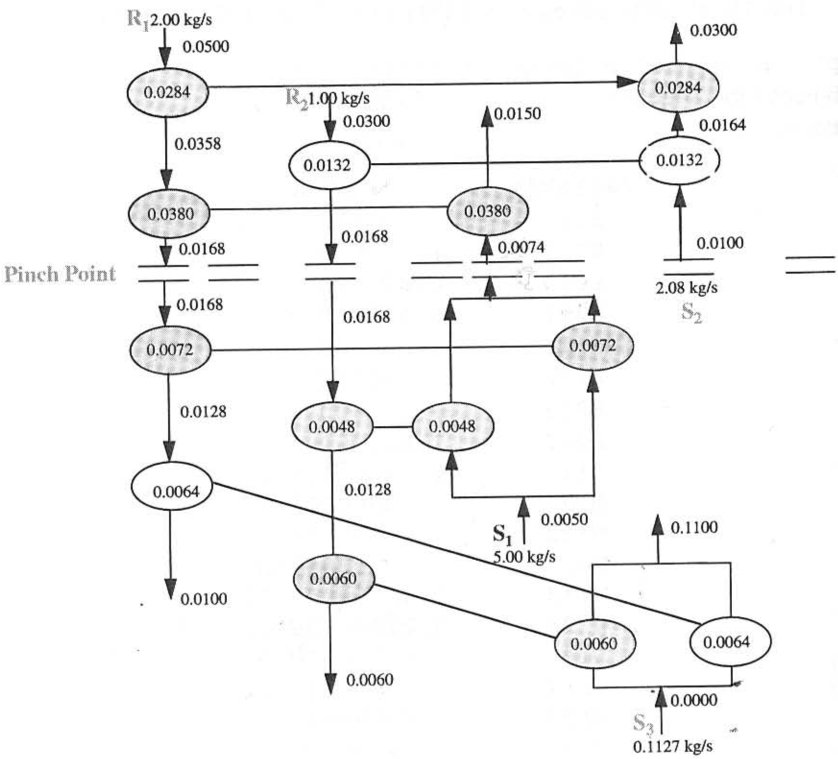

Figure 6.4 MOC network for dephenolization example.

instance, the transferable load from R_1 to S_2 above can be calculated as follows:

$$\begin{aligned}\text{Exchangeable load for } E_{1,2,1} &= W_{1,2,2} + W_{1,2,3} + W_{1,2,4} \\ &= 0.0210 + 0.0027 + 0.0047 \\ &= 0.0284 \text{ kg phenol/s}\end{aligned} \tag{6.15}$$

Hence, one can use these results to construct the network shown in Fig. 6.4. This is the same configuration obtained using the algebraic method as illustrated by Fig. 5.13. However, the loads below the pinch are distributed differently. This is consistent with the previously mentioned observation that multiple solutions featuring same objective function can exist for the problem. The final design should be based on considerations of total annualized cost, safety, flexibility, operability and controllability. As has been discussed in Sections 3.11 and 5.8, the minimum TAC can be attained by trading off fixed versus operating costs by optimizing driving forces, stream mixing and mass-load paths.

Problems

6.1 Using linear programming, resolve the dephenolization example presented in this chapter for the case when the two waste streams are allowed to mix.

6.2 Using mixed-integer programming, find the minimum number of mass exchangers the benzene recovery example described in Section 3.7 (Example 3.1).

6.3 Employ linear programming to find the MOC solution for the toluene-removal example described in Section 3.10 (Example 3.3).

6.4 Use optimization to solve problem 3.1.

6.5 Apply the optimization-based approach presented in this chapter to solve problem 3.3.

6.6 Employ linear programming to solve problem 3.4.

6.7 Solve problem 5.5 using optimization.

6.8 Consider the metal pickling plant shown in Fig. 6.5 (El-Halwagi and Manousiouthakis, 1990a). The objective of this process is to use a pickle solution (e.g., HCl) to remove corrosion products, oxides and scales from the metal surface. The spent pickle solution

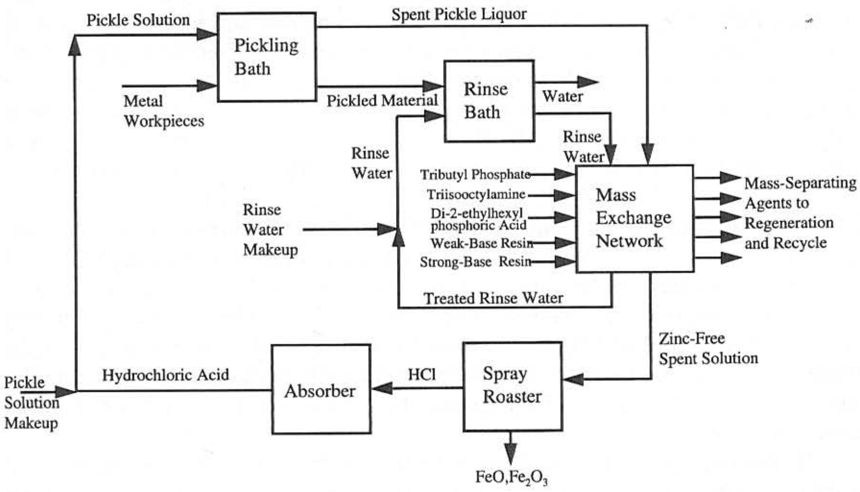

Figure 6.5 Zinc recovery from metal picking plant from (from El-Halwagi and Manousiouthakis, 1990a. Automatic Synthesis of MassExchange Networks, *Chem. Eng. Sci.*, 45(9), p. 2818, Copyright © 1990, with kind permission from Elsevier Science Ltd., The Boulevard, Langford Lane, Kidlington 0X5 1GB, UK.)

Table 6.11
Stream Data for the Zinc Recovery Problem

Rich stream				MSAs						
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	0.2	0.08	0.02	S_1		0.0060	0.0600	0.845	0.000	0.02
R_2	0.1	0.03	0.001	S_2		0.0100	0.0200	1.134	0.010	0.11
				S_3		0.0090	0.0500	0.632	0.020	0.04
				S_4		0.0001	0.0100	0.376	0.0001	0.05
				S_5		0.0040	0.0150	0.362	0.002	0.13

contains zinc chloride and ferrous chloride as the two primary contaminants. Mass exchange can be used to selectively recover zinc chloride from the spent liquor. The zinc-free liquor is then forwarded to a spray furnace in which ferrous chloride is converted to hydrogen chloride and iron oxides. The hydrogen chloride is absorbed and recycled to the pickling path. The metal leaving the pickling path is rinsed off by water to remove the clinging film of drag-out chemicals that adheres to the workpiece surface. The rinse wastewater contains zinc chloride as the primary pollutant that must be recovered for environmental and economic purposes.

The purpose of the problem is to systematically synthesize a cost-effective MEN that can recover zinc chloride from the spent pickle liquor, R_1, and the rinse wastewater, R_2. Two mass-exchange processes are proposed for recovering zinc; solvent extraction and ion exchange. For solvent extraction, three candidate MSAs are suggested: tributyl phosphate, S_1, triisooctyl amine, S_2, and di-2-ethyl hexyl phosphoric acid, S_3. For ion exchange, two resins are proposed: a strong-base resin, S_4, and a weak-base resin, S_5. Table 6.11 summarizes the data for all the streams. All compositions are given in mass fractions. Assume a value of 0.0001 for the minimum allowable composition difference for all lean streams.

6.9 Etching of copper, using an ammoniacal solution, is an important operation in the manufacture of printed circuit boards for the microelectronics industry. During etching, the concentration of copper in the ammoniacal solution increases. Etching is most efficiently carried out for copper concentrations between 10 and 13 w/w% in the solution while etching efficiency almost vanishes at higher concentrations (15–17 w/w%). In order to maintain the etching efficiency, copper must be continuously removed from the spent ammoniacal solution through solvent extraction. The regenerated ammoniacal etchant can then be recycled to the etching line.

The etched printed circuit boards are washed out with water to dilute the concentration of the contaminants on the board surface to an acceptable level. The extraction of copper from the effluent rinse water is essential for both environmental and economic reasons since decontaminated water is returned to the rinse vessel.

A schematic representation of the etching process is demonstrated in Fig. 6.6. The proposed copper recovery scheme is to feed both the spent etchant and the effluent rinse water

Table 6.12
Stream Data for the Copper Etching Problem

Rich streams				MSAs						
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	0.25	0.13	0.10	S_1	∞	0.030	0.070	0.734	0.001	0.01
R_2	0.10	0.06	0.02	S_2	∞	0.001	0.020	0.111	1.013	0.12

to a MEN in which copper is transferred to some selective solvents. Two extractants are recommended for this separation task: LIX63 (an aliphatic-hydroxyoxime), S_1, and P_1 (an aromatic-hydroxyoxime), S_2. The former solvent appears to work most efficiently at moderate copper concentrations, whereas the latter extractant offers remarkable extraction efficiencies at low copper concentrations. Table 6.12 summarizes the stream data for the problem.

Two types of contractors will be utilized: a perforated-plate column for S_1 and a packed column for S_2. The basic design and cost data that should be employed in this problem are given by El-Halwagi and Manousiouthakis (Chem. Eng. Sci., 45(9), p. 2831, 1990a).

It is desired to synthesizes an optimum MEN that features minimum total annualized cost, "TAC", where

$$\text{TAC} = \text{Annualized fixed cost} + \text{Annual operating cost.}$$

(Hint: vary the minimum allowable composition differences to iteratively trade off fixed versus operating costs).

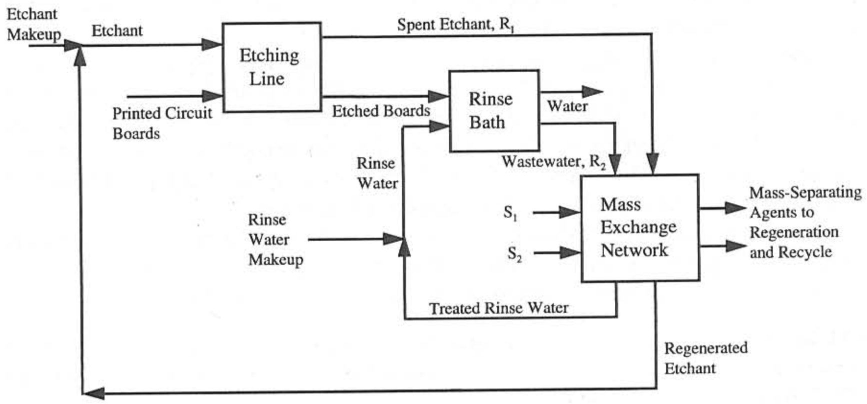

Figure 6.6 Recovery of Copper from Liquid Effluents of an Etching Plant (El-Halwagi and Manousiouthakis, 1990a. Automatic Synthesis of MassExchange Networks, *Chem. Eng. Sci.*, 45(9), p. 2825, Copyright © 1990, with kind permission from Elsevier Science Ltd., The Boulevard, Langford Lane, Kidlington 0X5 1GB, UK.)

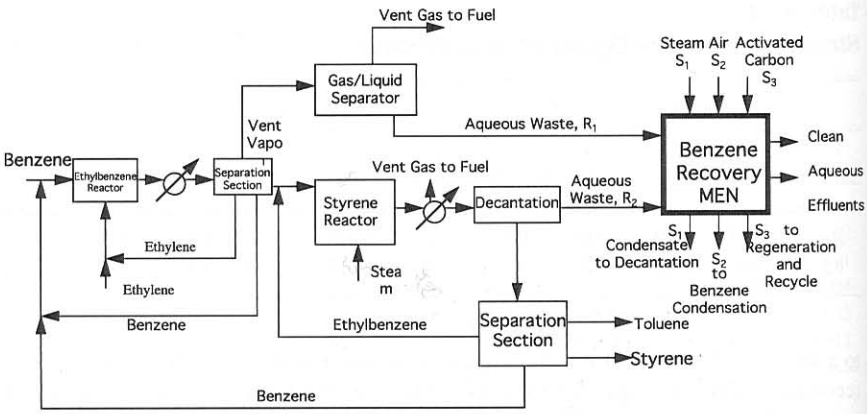

Figure 6.7 Schematic flowsheet of a styrene plant (Stanley and El-Halwagi, 1995, reproduced with permission of the McGraw Hill Companies).

6.10 Styrene can be produced by the dehydrogenation of ethylbenzene using live steam over an oxide catalyst at temperatures of 600°C to 650°C (Stanley and El-Halwagi, 1995). The process flowsheet is shown by Fig. 6.7. The first step in the process is to convert ethylene and benzene into ethylbenzene. The reaction products are cooled and separated. One of the separated streams is an aqueous waste (R_1). The main pollutant in this stream is benzene. Ethylbenzene leaving the separation section is fed to the styrene reactor whereby styrene and hydrogen are formed. Furthermore, by products (benzene, ethane, toluene and methane) are generated. The reactor product is then cooled and decanted. The aqueous layer leaving the decanter is a wastewater stream (R_2) which consists of steam condensate saturated with benzene. The organic layer, consisting of styrene, benzene, toluene, and unreacted ethylbenzene, is sent to a separation section.

There are two primary sources for aqueous pollution in this process—the condensate streams R_1 (1,000 kg/hr) and R_2 (69,500 kg/hr). Both streams have the same supply composition, which corresponds to the solubility of benzene in water which is 1770 ppm (1.77×10^{-3} kg benzene/kg water). Consequently, they may be combined as a single stream. The target composition is 57 ppb as dictated by the VOC environmental regulations called NPDES (National Pollutant Discharge Elimination System).

Three mass-exchange operations are considered: steam stripping, air stripping and adsorption using granular activated carbon. The stream data are given in Table 6.13.

Using linear programming, determine the MOC solution of the system.

6.11 In the previous problem, it is desired to compare the total annualized cost of the benzene-recovery system to the value of recovered benzene. The total annualized cost "TAC" for the network is defined as:

$$\text{TAC} = \text{Annual operating cost} + 0.2 \times \text{Fixed capital cost.}$$

The fixed cost($) of a moving-bed adsorption or regeneration column is given by $30{,}000V^{0.57}$, where V is the volume of the column (m^3) based on a 15-minute residence

Table 6.13
Data of the MSAs in Styrene Plant Problem

Stream	L_j^C (kg/s)	Supply composition x_j^s	Target composition x_j^t	m_j	ε_j	C_j ($/kg MSA)
Stream (S_1)	∞	0	1.62	0.5	0.15	0.004
Air (S_2)	∞	0	0.02	1.0	0.01	0.003
Carbon(S_3)	∞	3×10^{-5}	0.20	0.8	5×10^{-5}	0.026

All compositions and equilibrium data are in **mass ratios,** kg benzene/kg benzene-free MSA.

time for the combined flowrate of carbon and wastewater (or steam). A steam stripper already exists on site with its piping, ancillary equipment and instrumentation. The column will be salvaged for benzene recovery. The only changes needed involve replacing the plates inside the column with new sieve trays. The fixed cost of the sieve trays is $1,750/plate. The overall column efficiency is assumed to be 65%.

If the value of recovered benzene is taken as $0.20/kg, compare the annual revenue from recovering benzene to the TAC of the MEN.

6.12 In many situations, there is a trade-off between reducing the amount of generated waste at the source versus its recovery via a separation system. For instance, in problem 6.10, live steam is used in the styrene reactor to enhance the product yield. However, the steam eventually constitutes the aqueous waste, R_2. Hence, the higher the flowrate of steam, the larger the cost of the benzene recycle/reuse MEN. These opposing effects call for the simultaneous consideration of source reduction of R_2 along with its recycle/reuse. One way of approaching this problem is by invoking economic criteria. Let us define the economic potential of the process ($/yr) as follows (Stanley and El-Halwagi, 1995):

$$\begin{aligned}\text{Economic potential} = {} & \text{Value of produced styrene} \\ & + \text{Value of recovered ethylbenzene} \\ & - \text{Cost of Ethylbenzene} - \text{Cost of Steam} \\ & - \text{TAC of the recycle/reuse network}\end{aligned}$$

Determine the optimal steam ratio (kg steam/kg ethylbenzene) that should be used in the styrene reactor in order to maximize the economic potential of the process.

Symbols

- C_j unit cost of the jth MSA including regeneration and makeup, $/kg of recirculating MSA)
- d_j index for substreams of the jth MSA
- $E_{i,j,m}$ a binary integer variable designating the existence or absence of an exchanger between rich stream i and lean stream j in subnetwork m

G_i	flowrate of the ith waste stream
i	index of waste streams
j	index of MSAs
k	index of composition intervals
L_j	flowrate of the jth MSA(kg/s)
L_j, d_j	flowrate of substream of d_j the jth MSA(kg/s)
L_{j^c}	upper bound on available flowrate of the jth MSA(kg/s)
m	subnetwork (one above the pinch and two below the pinch)
m_j	slope of equilibrium line for the jth MSA
N_{int}	number of composition intervals
N_R	number of waste streams
N_S	number of MSAs
ND_j	Number of substreams for the jth MSA
R_i	the ith waste stream
R_m	a set defined by Eq. 6.9
$R_{m,k}$	a set defined by Eq. 6.11
S_j	the jth MSA
S_m	a set defined by Eq. 6.10
$S_{m,k}$	a set defined by Eq. 6.12
SN_m	subnetwork m
$U_{i,j,m}$	upper bound on exchangeable mass between i and j in subnetwork m (defined by Eq. 6.13)(kg/s)
$W_{i,j,k}$	exchangeable load between the ith waste stream and the jth MSA in the kth interval (kg/s)
$W^R_{i,k}$	exchangeable load of the ith waste stream which passes through the kth interval as defined by Eqs. (6.2) and (6.3) (kg/s)
$w^S_{j,k}$	exchangeable load of the jth MSA which passes through the kth interval as defined by Eqs. (6.5) and (6.6) (kg/s)
W^R_k	the collective exchangeable load of the waste streams in interval k as defined by Eq. (6.4) (kg/s)
$x_{j,k-1}$	composition of key component in the jth MSA at the upper horizontal line defining the kth interval
$x_{j,k}$	composition of key component in the jth MSA at the lower horizontal line defining the kth interval
x^{out}_j	outlet composition of the jth MSA (defined by Eq. 6.8)
x^s_j	supply composition of the jth MSA
x^t_j	target composition of the jth MSA
y_{k-1}	composition of key component in the ith waste stream at the upper horizontal line defining the kth interval
y_k	composition of key component in the ith waste stream at the lower horizontal line defining the kth interval

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