Appendix D

Mass/Heat Exchange Hyperstructure Model for Acetone Recovery Example

The mass/heat exchange hyperstructure in the acetone recovery example involves 4 mass/heat transfer blocks and 11 pure heat exchangers (see Figure 8.1). The synthesis model involves:

- Mass balances for total stream flows
  - at initial stream splitters, *e.g.* at the initial splitter of PA.

    $$F_{PA}^{IN} = f_{PA,PA-LP}^{Rin} + f_{PA,PA-LW}^{Rin}$$

    where F_{PA}^{IN} is the total flow of air mixture and $f_{PA,PA-LP}^{Rin}$, $f_{PA,PA-LW}^{Rin}$ the flows towards its potential exchangers (see Figure 8.1).
  - at stream splitters at the outlet of each exchange block (mass/heat or pure heat), *e.g.* at the lean side splitter after $PA-LW$.

    $$\begin{aligned} f_{PA-LW}^{L,out} = {} & f_{LW-VW}^{LBR,PA-LW} + f_{LP-VP}^{LBR,PA-LW} + f_{PA-LP}^{LBL,PA-LW} + f_{PA-LW}^{LBL,PA-LW} + \\ & f_{LP-LP}^{LBH,PA-LW} + f_{LP-LW}^{LBH,PA-LW} + f_{LP-CW}^{LBH,PA-LW} + f_{LW-LP}^{LBH,PA-LW} + \\ & f_{LW-LW}^{LBH,PA-LW} + f_{LW-CW}^{LBH,PA-LW} + f_{LP-LP}^{LBC,PA-LW} + f_{VP-LP}^{LBC,PA-LW} + \\ & f_{LW-LP}^{LBC,PA-LW} + f_{LP-LW}^{LBC,PA-LW} + f_{VP-LW}^{LBC,PA-LW} + f_{LW-LW}^{LBC,PA-LW} + \\ & f_{S-LW}^{LBC,PA-LW} + f_{LP}^{LO,PA-LW} + f_{LW}^{LO,PA-LW} \end{aligned}$$

    where $f_{PA-LW}^{L,out}$ is the flow out of the lean side of exchanger (PA-LW), $f_{LW-VW}^{LBR,PA-LW}$ is the bypass flow from the Lean side of (PA-LW) to the Rich side of (LW-VW) and so on. The above flows are possible according to phase-mixing assumptions. However, some of them, *e.g.* $f_{LP-LP}^{LBC,PA-LW}$, which seem improbable, are eliminated by optimization.

– at mixers prior to heat exchanger sides (mass/heat or pure heat), *e.g.* at the lean side mixer prior to $PA-LW$.

$$\begin{aligned} f_{PA-LW}^{L,in} = & f_{PA-LW}^{LBL,PA-LP} + f_{PA-LW}^{RBL,LW-VW} + f_{PA-LW}^{RBL,LP-VW} + f_{PA-LW}^{HBL,LP-LP} + \\ & f_{PA-LW}^{HBL,LP-LW} + f_{PA-LW}^{HBL,LP-CW} + f_{PA-LW}^{HBL,LW-LP} + f_{PA-LW}^{HBL,LW-LW} + \\ & f_{PA-LW}^{HBL,LW,CW} + f_{PA-LW}^{CBL,LP-LP} + f_{PA-LW}^{CBL,VP,LP} + f_{PA-LW}^{CBL,LW-LP} + \\ & f_{PA-LW}^{CBL,S-LP} + f_{PA-LW}^{CBL,LP-LW} + f_{PA-LW}^{CBL,VP-LW} + f_{PA-LW}^{CBL,LW-LW} + \\ & f_{PA-LW}^{CBL,S-LW} + f_{W,PA-LW}^{Lin} \end{aligned}$$

where $f_{PA-LW}^{L,in}$ is the flow into the lean side of exchanger (PA-LW) and the rest flows are defined as above.

– at final mixers, *e.g.* at the final mixer of acetone-rich liquid product:

$$\begin{aligned} F_{LP}^{OUT} = & f_{LP,PA-LW}^{LO} + f_{LP,PA-LP}^{LO} + f_{LP,LP-VP}^{RO} + f_{LP,LW-VW}^{RO} + \\ & f_{LP,LP-LP}^{HO} + f_{LP,LP-LW}^{HO} + f_{LP,LP-CW}^{HO} + f_{LP,LW-LP}^{HO} + \\ & f_{LP,LW-LW}^{HO} + f_{LP,LW-CW}^{HO} + f_{LP,LP-LP}^{CO} + f_{LP,VP-LP}^{CO} + \\ & f_{LP,LW-LP}^{CO} + f_{LP,S-LP}^{CO} + f_{LP,LP-LW}^{CO} + f_{LP,VP-LW}^{CO} + \\ & f_{LP,LW-LW}^{CO} + f_{LP,S-LW}^{CO} \end{aligned}$$

where F_{LP}^{OUT} is the desired product flow, $f_{LP,PA-LW}^{LO}$ the flow out from the lean side of PA-LW towards the final mixers of LP, etc.

- Component mass balances, similarly to total flow mass balances at:
  – mixers prior to each exchanger side, to determine inlet compositions to the corresponding exchanger side
  – final mixers of streams, to determine outlet compositions.
- Mass balances for each component at each mass/heat exchanger block, *e.g.* for acetone at PA-LW:

$$f_{PA-LW}^{Lin} x_{PA-LW}^{Lin,acet} + f_{PA-LW}^{Rin} x_{PA-LW}^{Rin,acet} - f_{PA-LW}^{Rout} x_{PA-LW}^{Rout,acet} - f_{PA-LW}^{Lout} x_{PA-LW}^{Lout,acet} + \mathcal{F}(reactions)$$

where $x's$ are compositions, correspondingly to flows and $\mathcal{F}(reactions)$ accounts for possible generation or consumption of acetone, if any reactions are known to take place in a (PA-LW) system.

- Summation of molar fractions (equal to 1) at each mass/heat exchanger outlet.

- Enthalpy balances at the mixers of the hyperstructure, to determine the mixer outlet temperature.
- Enthalpy balances at each mass/heat exchange block, where reaction enthalpy and/or phase change enthalpy are taken into considerations.
- Energy balances at each heat exchange block, accounting for phase-change enthalpy.
- Phase-defining constraints at the hyperstructure mixers and each exchanger outlet, *e.g.* at the outlet of rich side of (LW-VW):

$$x_{LW-VW}^{Lout,acet} k_{LW-VW}^{Lout,acet} + x_{LW-VW}^{Lout,water} k_{LW-VW}^{Lout,water} \leq 1$$

  where k's define phase equilibrium constants (note that air may not be possible in this mixture, at moderate conditions).
- Temperature driving force constraints at heat exchangers

The existence of each mass/heat and pure heat transfer block is denoted by a binary variable. Any air-liquid mass transfer block is sized as an absorption tower and Kremser equation (Douglas, 1988) is employed:

$$N_{ij} = \frac{ln\left(\left(1 - \frac{m_{ijc} f_{ij}^R}{f_{ij}^L}\right) \frac{(x_{ij}^{Rin,c} - m_{ijc} x_{ij}^{Lin,c} - b_{ijc})}{(x_{ij}^{Rout,c} - m_{ijc} x_{ij}^{Lin,c} - b_{ijc})} + \frac{m_{ijc} f_{ij}^R}{f_{ij}^L}\right)}{ln\left(\frac{m_{ijc} f_{ij}^R}{f_{ij}^L}\right)}$$

where N_{ij} is the number of absorption trays corresponding to the mass/heat exchange match between (i, j), f_{ij}^R and f_{ij}^L are average flowrates of the rich and the lean sides respectively, $x_{ij}^{Rin,c}$, $x_{ij}^{Rout,c}$, $x_{ij}^{Lin,c}$ inlet and outlet compositions of the transferred component c, accordingly and m_{ijc} and b_{ijc} constants that govern the mass transfer.

The arrangement of two liquid-vapour mass transfer blocks, connected counter-currently at the lean and the rich sides, which is identified through integer constraints on decision/structural variables accounting for block interconnections, is sized as a conventional distillation column, based on Fenske and Underwood equations, with the simplifying assumptions of:

$$N = 2N_{min}$$

$$R = 1.2R_{min}$$

where N is the number of trays, N_{min} the minimum number of trays, R the reflux ratio and R_{min} the minimum reflux ratio, calculated from:

$$N_{min} = \frac{ln\left[\left(\frac{x_{top}^{Lin,acet}}{(1 - x_{top}^{Lin,acet})}\right)\left(\frac{x_{bottom}^{Rout,acet}}{(1 - x_{bottom}^{Rout,acet})}\right)\right]}{ln\alpha}$$

where $x_{top}^{Lin,acet}$, $x_{bottom}^{Rout,acet}$ account for top and bottom acetone compositions at the column and α for relative volatility.

$$R_{min} = \left(\frac{1}{\alpha - 1}\right)\left[\frac{x_{top}^{Lin,acet}}{x_f^{acet}} - \frac{\alpha(1 - x_{top}^{Lin,acet})}{1 - x_f^{acet}}\right]$$

where x_f^{acet} is the feed acetone composition.

The resulting MINLP model features 848 rows, 544 continuous variables and 127 binary variables (16 corresponding to mass/heat and heat exchange blocks). The model was solved employing Generalized Benders Decomposition through the modelling system GAMS. Starting from the structure illustrated in Figure 8.3, the solution was obtained in 6 GBD iterations.