SUPPLEMENTARY MATERIAL

Globally Optimal Distillation Column Design using Set Trimming and Enumeration Techniques

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PART A

Mixed-Integer Nonlinear Model – Example 1

(Luyben and Floudas, 1994)

Example 1 of the paper corresponds to the distillation design problem present in Luyben and Floudas (1994). The constraints and the objective function of the corresponding MINLM are presented below, where binary variables (w) represent if a given tray exists or not.

Sequential tray constraints:

$$w_n - w_{n+1} \leq 0 \qquad \forall\, n \in AF \tag{SA-1}$$

$$w_n - w_{n-1} \leq 0 \qquad \forall\, n \in BF \tag{SA-2}$$

$$w_{Nf} = 1 \tag{SA-3}$$

Material balance constraints:

$$V^R y_1 w_1 + L^R x_1 - V^R y_2 w_1 - L^R x_D = 0 \tag{SA-4}$$

$$V^R y_n w_n + L^R x_n - V^R y_{n+1} w_n - L^R x_{n-1} = 0 \qquad \forall\, n \in AF^* \tag{SA-5}$$

$$V^R y_{Nf} + L^S x_{Nf} - L^R x_{Nf-1} - V^S y_{Nf+1} - \hat{F}\hat{z} = 0 \tag{SA-6}$$

$$V^S y_n w_n + L^S x_n - L^S x_{n-1} - V^S y_{n+1} w_n = 0 \qquad \forall\, n \in BF^* \tag{SA-7}$$

$$V^S y_{Nt} w_{Nt} + L^S x_{Nt} - L^S x_{Nt-1} - V^S y_B w_{Nt} = 0 \tag{SA-8}$$

$$V^A - V^B - \widehat{F_V} = 0 \tag{SA-9}$$

$$L^B - L^A - \widehat{F_L} = 0 \tag{SA-10}$$

Total condenser:

$$V^A - L^A - \widehat{D} = 0 \tag{SA-11}$$

$$y_1 - \widehat{x_D} = 0 \tag{SA-12}$$

Reboiler:

$$B + V^B - L^B = 0 \tag{SA-13}$$

$$B x_B + V^B y_B - L^B x_{Nt} = 0 \tag{SA\_14}$$

Phase equilibrium constraints:

$$\hat{\alpha} x_n - y_n[1 + x_n(\hat{\alpha} - 1)]w_n - \widehat{x_D}\hat{\alpha}(1 - w_n) = 0 \qquad \forall\, n = 1 \tag{SA-15}$$

$$\hat{\alpha} x_n - y_n[1 + x_n(\hat{\alpha} - 1)]w_n - x_{n-1}\hat{\alpha}(1 - w_n) = 0 \qquad \forall\, n = 2, \dots, Nt \tag{SA-16}$$

$$\hat{\alpha} x_B - y_B[1 + x_B(\hat{\alpha} - 1)] = 0 \tag{SA-17}$$

Column diameter constraint:

$$D_{col}^2 - \frac{4\, Vb\, \widehat{MW}}{\pi \hat{v} \widehat{\rho_V}} = 0 \tag{SA-18}$$

where: $\hat{v} = \widehat{k_v}\, \widehat{ff} \sqrt{\frac{\widehat{\rho_L} - \widehat{\rho_V}}{\widehat{\rho_V}}}$

Product specification constraint:

$$x_D - \widehat{x_D}^{spec} \geq 0 \tag{SA-19}$$

$$x_B - \widehat{x_B}^{spec} \leq 0 \tag{SA-20}$$

Objective function:

$$N_{tray} = \sum_n w_n \tag{SA-21}$$

$$Cost = \beta_{tax}\left(C_{LPS}\Delta H_{vap} + C_{CW}\Delta H_{cond}\right)Vb + f/\beta_{pay} \tag{SA-22}$$

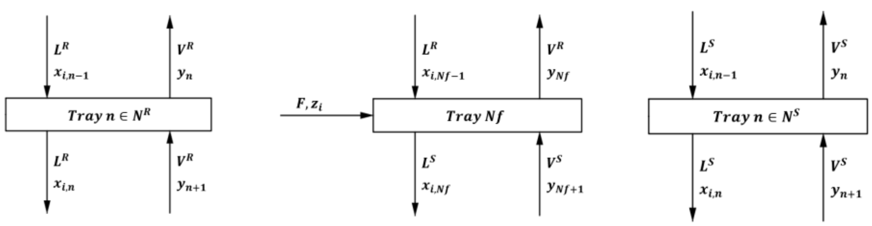
$$f = 12.3\left[615 + 324\, D_{col}^2 + 486(6 + 0.76 Ntray)D_{col}\right] + 245 N_{tray}(0.7 + 1.5\, D_{col}^2) \tag{SA-23}$$

PART B

Distillation Model Based on the Equimolar Flow Assumption

This section presents a distillation mathematical model equivalent to the optimization problem formulation of Luyben and Floudas (1994), present in the previous section. This model is used in the Set Trimming followed by Enumeration procedure for the solution of the design problem in Example 1 of the paper. The goal is to compare the performance of the proposed approach with mathematical programming.

The model equations involve material balances, equilibrium relations and, diameter calculations. The material balance for each tray ($n \in N$) is illustrated in Figure 1. Sets N^R and N^S are subsets of N, whose elements are trays of the rectifying and stripping sections, respectively, and Nf represents the feed tray location.



(a) (b) (c)

Figure SB1: Material balances on (a) tray $n \in N^R$, (b) tray $n = Nf$ and (c) tray $n \in N^S$.

The material balances for components $i \in I' = \{1, 2, \ldots, Nc\text{-}1\}$ are represented in Eqs. (SB-1) to (SB-5) and the overall balance in the feed tray in Eqs. (SB-6) and (SB-7):

$$V^R y_{i,1} + L^R x_{i,1} - V^R y_{i,2} - L^R x_{D_i} = 0 \qquad \forall\, i \in I' \tag{SB-1}$$
$$V^R y_{i,n} + L^R x_{i,n} - V^R y_{i,n+1} - L^R x_{i,n-1} = 0 \qquad \forall\, n \in N^R, \forall\, i \in I' \tag{SB-2}$$
$$V^R y_{i,Nf} + L^S x_{i,Nf} - V^S y_{i,Nf+1} - L^R x_{i,Nf-1} - \hat{F}\ \hat{z}_i = 0 \qquad \forall\, i \in I' \tag{SB-3}$$
$$V^S y_{i,n} + L^S x_{i,n} - L^S x_{i,n-1} - V^S y_{i,n+1} = 0 \qquad \forall\, n \in N^S, \forall\, i \in I' \tag{SB-4}$$
$$V^S y_{i,Nt} + L^S x_{i,Nt} - L^S x_{i,Nt-1} - V^S y_{B_i} = 0 \qquad \forall\, i \in I' \tag{SB-5}$$
$$V^R - V^S - \widehat{F_V} = 0 \tag{SB-6}$$
$$L^S - L^R - \widehat{F_L} = 0 \tag{SB-7}$$

For the total condenser and the equilibrium reboiler, the material balance is given by:

$$y_{i,1} - x_{D_i} = 0 \qquad \forall\, i \in I' \tag{SB-8}$$

$$V^R - L^R - D = 0 \qquad \text{(SB-9)}$$
$$L^S x_{i,Nt} - B\, x_{B_i} - V^S y_{B_i} = 0 \qquad \forall\, i \in I' \qquad \text{(SB-10)}$$
$$L^S - B - V^S = 0 \qquad \text{(SB-11)}$$

Finally, the required summation equations are:

$$\textstyle\sum_i y_{i,n} = 1 \qquad \forall\, n \in N \qquad \text{(SB-12)}$$
$$\textstyle\sum_i x_{i,n} = 1 \qquad \forall\, n \in N \qquad \text{(SB-13)}$$
$$\textstyle\sum_i x_{D_i} = 1 \qquad \text{(SB-14)}$$
$$\textstyle\sum_i x_{B_i} = 1 \qquad \text{(SB-15)}$$
$$\textstyle\sum_i y_{B_i} = 1 \qquad \text{(SB-16)}$$

We use the relative volatilities that are constant throughout the column: $\widehat{\alpha_{i,j}} = K_i/K_j = (y_i/x_i)/(y_j/x_j)$. Therefore, the equilibrium relations can be written as follows:

$$x_{i,n} = \left(\frac{y_{i,n}}{\widehat{\alpha_{i,NC}}\,(y_{NC,n}/x_{NC,n})}\right) \qquad \forall\, n \in N, \forall\, i \in I' \qquad \text{(SB-17)}$$
$$x_{B_i} = \left(\frac{y_{B_i}}{\widehat{\alpha_{i,NC}}\,(y_{B_{NC}}/x_{B_{NC}})}\right) \qquad \forall\, i \in I' \qquad \text{(SB-18)}$$

The diameter and cost calculation are given by:

$$D_{col}^2 - \frac{4\, V^S\, \widehat{MW}}{\pi\left(\widehat{k_v}\,\widehat{ff}\,\sqrt{\frac{\widehat{\rho_L}-\widehat{\rho_V}}{\widehat{\rho_V}}}\right)\widehat{\rho_V}} = 0 \qquad \text{(SB-19)}$$
$$Cost = \widehat{\beta_{tax}}\left(\widehat{C_{LPS}}\,\widehat{\Delta H_{vap}} + \widehat{C_{CW}}\,\widehat{\Delta H_{cond}}\right)V^S + \left\{12.3\left[615 + 324\ D_{col}^2 + 486(6 + 0.76\,Nt)D_{col}\right] + 245Nt\left(0.7 + 1.5\,D_{col}^2\right)\right\}/\widehat{\beta_{pay}} \qquad \text{(SB-20)}$$

If the number of trays (*Nt*) and the feed tray location (*Nf*) are fixed to represent a given solution candidate, then all other variables can be calculated.

PART C

MESH Distillation Mathematical Model

The enumeration methods were also employed in a more rigorous distillation column model, addressed in Example 2. The model describes the column as a set of equilibrium stages. The equations that underpin the model are based on the total and component material balance (M), the equilibrium relations (E), the summation equations (S), and the enthalpy balances (H), forming the acronym MESH. A scheme of a given equilibrium stage is shown in Figure SC-1.

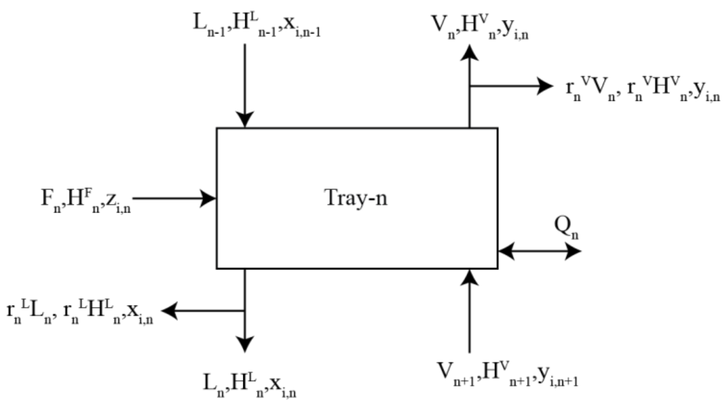


Figure SC-1: General stage representation for the MESH formulation.

The material balances for components $i \in \mathrm{I} = \{1, 2, \ldots, Nc\}$ at stage $n \in N = \{1, 2, \ldots, N_t\}$ are represented by:

$$(1 + r_n^V)V_n y_{i,n} + (1 + r_n^L)L_n x_{i,n} - V_{n+1} y_{i,n+1} - L_{n-1} x_{i,n-1} - F_n z_{i,n} = 0 \qquad \forall\, n \in N, \forall\, i \in I \qquad \text{(SC-1)}$$

where r_n^V and r_n^L are the ratio of the side product flow to the main tray flow for the vapor (V_n) and liquid (V_n), respectively.

The condenser and reboiler are defined as the tray 0 and tray N_t+1, respectively. It was assumed the total condenser, and an equilibrium reboiler and their particular component balances are represented in Eqs (SC-2) for the condenser and (SC-4) for the reboiler.

$$(L_0 + D)x_{i,0} - V_1 y_{i,1} = 0 \qquad \forall\, i \in I \qquad \text{(SC-2)}$$
$$V_{N_t+1} y_{i,N_t,1} + L_{N_t+1} x_{i,N_t+1} - L_{Nt} x_{i,N_t} = 0 \qquad \forall\, i \in I \qquad \text{(SC-3)}$$

The equilibrium relations for the stage are given by:

$$K_{i,n} = \frac{y_{i,n}}{x_{i,n}} = \frac{\gamma_{i,n}\, P_{i,n}^{SAT}(T_n)}{\phi_{g_{i,n}} P_n} \quad \forall\, n \in N, n = N_t + 1 \quad \forall\, i \in I \tag{SC-4}$$

where $K_{i,j}$ vapor-liquid equilibrium ratio, the $\gamma_{i,n}$ is the activity coefficient (the NRTL model is used), $\phi_{g_{i,n}}$ is the gas fugacity coefficient from the Peng-Robinson equation of state, $P_{i,n}^{SAT}$ is the saturation pressure of component i , in tray n and P_n is the column pressure at tray n.. The saturation pressures are a function of the temperature of the tray (T_n), which is a variable of the model.

The summation equations are given by:

$$\sum_{i=1}^{N_c} y_{i,n} - 1 = 0 \qquad \forall\, n \in N, n = N_t + 1 \tag{SC-5}$$
$$\sum_{i=1}^{N_c} x_{i,n} - 1 = 0 \qquad \forall\, n \in N, n = 0, N_t + 1 \tag{SC-6}$$

The enthalpy balance for each stage, the reboiler and the condenser is given by.

$$\begin{aligned}(1 + r_n^V)V_n H_n^V(T_n) + (1 + r_n^L)L_n H_n^L(T_n) + Q_n - V_{n+1}H_{n+1}^V(T_n) \\ - L_{n-1}H_{n-1}^L(T_n) - F_n H_n^F(T_n^F) = 0 \quad n \in N\end{aligned} \tag{SC-7}$$
$$V_{n+1}H_{n+1}^V(T_n) - Q_{n+1} - BH_{n+1}^L = 0 \tag{SC-8}$$
$$V_1 H_1^V - Q_0 - (L_0 + D)H_0^L = 0 \tag{SC-9}$$

The cost of equipment and utilities is estimated following the methodology of Douglas (1988), Elliot and Luyben (1996), and Cheng et al. (2009). It was assumed a payback of 3 years and we used a M&S index of 1773.4 (Roux et al., 2022; Douglas, 1988). The reboiler (A_R) and condenser area (A_C) are evaluated by Equations S50 and S51, respectively, with $U_C = 852\ \mathrm{W/(m^2K)}$ and $U_R = 1419.56\ \mathrm{W/(m^2K)}$ (Douglas, 1988).

$$A_R[\mathrm{m}^2] = \frac{Q_R}{U_R \Delta T^R} \tag{SC-10}$$
$$A_C[\mathrm{m}^2] = \frac{Q_c}{U_c \Delta T_{lm}^C} \tag{SC-11}$$

The column diameter is given by the following equation, where V_{MAX} is the maximum vapor-flowrate (kmol/h), v_g is the gas molar volume ($\mathrm{m^3/kmol}$) and M_W is the molecular weight (kg/kgmol).

$$D_C[\mathrm{m}] = \sqrt{\frac{6.9\cdot 10^{-4}[h\ m^{1/2} kg^{-1/2}]}{\pi}\left(M_W v_g\right)^{\frac{1}{2}} V_{MAX}} \tag{SC-12}$$

The column length (L_C) is dependent on the number of plates (N_t) by:

$$L_C[m] = 0.7315\, N_t \tag{SC-13}$$

With the equipment properly sized, one can estimate the Equipment cost. The column and tray cost following equations:

$$Column\ Cost\ [\$] = \frac{M\&S}{280}\left(101.9 D_C^{1.066} L_C^{0.802}\left(2.18 + (3.67 + 1.2)\right)\right) \quad \text{(SC-14)}$$

$$Tray\ cost\ [\$] = \frac{M\&S}{280}\left(4.7 D_C^{1.55} L_C (1 + 0.0 + 1.7)\right) \quad \text{(SC-15)}$$

The heat exchanger cost is given by Equation S56:

$$Heat\ exchanger\ cost\ [\$] = \frac{M\&S}{280} 101.3 (A_C^{0.65} + A_R^{0.65}) \times (2.29 + (1.35 + 0.1) \times 3.75) \quad \text{(SC-16)}$$

The utility costs are calculated by the following equations for the steam and cooling water, respectively.

$$Steam\ cost\ [\$/\text{year}] = 2.78 \times 10^{-6} \frac{\$}{\text{kJ}} Q_R 8150 \frac{\text{h}}{\text{year}} \quad \text{(SC-17)}$$

$$Cooling\ water\ cost\ [\$/\text{year}] = 2.78 \times 10^{-6} \frac{\$}{\text{kJ}} Q_C 8150 \frac{\text{h}}{\text{year}} \quad \text{(SC-18)}$$

The price of low-pressure steam ($160°C$, 5 barg) was assumed to be 2.78 $\$/\text{GJ}$ and for the cooling water (30 °C) it was 0.378 $\$/\text{GJ}$ (Turton et al., 2018).

NOMENCLATURE

$\widehat{\alpha_{i,j}}$	Relative volatility
β_{pay}	The payback period
β_{tax}	Tax factor
$\widehat{\Delta H_{vap}}$	Enthalpy of vaporization
$\widehat{\Delta H_{cond}}$	Enthalpy of condensation
ΔT^R	Temperature difference at the reboiler (K)
ΔT_{lm}^C	Logarithmic mean temperature difference at the condenser (K)
γ_{in}	Activity coefficient of component *i* at stage *n*
ϕ_{in}	Gas fugacity coefficient of component *i* at stage *n*
$\widehat{\rho_V}, \widehat{\rho_L}$	Liquid and vapor densities
A_R, A_C	Reboiler and area (m^2)
B	Bottom product flow rate (mol/min)
$\widehat{C_{LPS}}, \widehat{C_{CW}}$	Cost coefficients
D	Distillate product flow rate (mol/min)
$Dcol$	Tower diameter (*m*)
$\hat{F}$	Feed flowrate (mol/min)
$\widehat{F_V}$	Vapor Phase Feed flow rate (mol/min)
$\widehat{F_L}$	Liquid Phase Feed flow rate (mol/min)
F_n	Feed flowrate at stage n (kmol/h)
$\widehat{ff}$	Flooding factor
H_n	Molar enthalpy at stage *n* (kJ/kmol)
K_{in}	Partition coefficient of component i at stage n

$\widehat{k_v}$	Tray spacing flow
L^A, L^B	Liquid flow rate above and below feed (mol/min)
L_c	Column length (m)
L_n	Liquid molar flowrate leaving stage n (kmol/h)
L^R	Liquid flow rate above the feed (mol/min)
L^S	Liquid flow rate below the feed (mol/min)
M&S	Marshall and Swift Cost Index
$\widehat{MW}$	Molecular weight
Nc	Number of components
Nf	Feed tray
N^R	Total number of trays in the rectification section
N^S	Total number of trays in the stripping section
Nt	Total number of trays
rec_{ben}^{Top}	Recovery of benzene on the top of the column
rec_{tol}^{Bottom}	Recovery of Toluene on the bottom of the column
r_{in}	Flow ratio that is removed from each stage *n*
$P^{SAT}_{i.n}$	Vapor pressure of component *i* at stage *n*
P_n	Comlumn pressure at stage n (kPa)
Q_R,Q_C	Reboiler and Condenser duty (kJ/h)
TAC	Total anualized cost ($/yr)
U_R,U_C	Global heat transfer coefficient for the Reboiler (R) and Condenser (C)
V^A, V^B	Vapor flow rate above and below feed (mol/min)
v_g	Vapor molar volume (m^3/kmol)
V_{MAX}	Maximum vapor flowrate (kmol/h)
V_n	Vapor molar flowrate leaving stage n (kmol/h)
V^R	Vapor flow rate above the feed (mol/min)
V^S	Vapor flow rate below the feed (mol/min)
TAC	Total anualized costg
x_{B_i}	Bottom product molar fraction for component *i*
x_{D_i}	Distillate product molar fraction for component *i*
$x_{i,n}$	Liquid molar fraction for component *i* leaving tray *n*
y_{B_i}	Vapor boil-up molar fraction for component *i*
$y_{i,n}$	Vapor molar fraction for component *i* leaving tray *n*
$\hat{z}_i$	Feed molar fraction for component *i*
w	Equal to 1 if the tray exists
Subscripts	
i	Component
LK, HK	Light and heavy key components
n	Column tray
Superscript	
L	Liquid phase
spec	Specified variable
V	Vapor phase

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