OPTIMAL SYNTHESIS OF LIQUID-LIQUID MULTISTAGE EXTRACTORS

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Optimal Synthesis of Liquid-Liquid Multistage Extractors

- ***Objective***

To develop the optimal synthesis of liquid-liquid multistage extractors using Generalized Disjunctive Programming (GDP)

- ***Introduction***

- ***Design of Extraction Sequences***

- ***Problem Statement***

- ***General Superstructure***

- ***Generalized Disjunctive Programming Model***

- ***Solution Algorithm***

- ***Numerical Examples***

Design of a Extraction Sequence (crosscurrent and multistage):

Determination of the number of stages and solvent flow required for a desired separation (purity and/or recovery).

R= Raffinate phase {R(0)= feed stream to be separated}

E= Extract phase {E(0)= solvent feed}

Ternary systems

— Binodal curve
— Tie line
— Operative line

Note: “In the liquid-liquid equilibrium the existence of the two phases in equilibrium is not in the whole range of compositions”.

Quaternary systems

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• Problem Statement

Given is:

- a set of feed streams with known composition,
- a specified separation and/or recovery of solutes in the product stream.

The design problem consists of determining:

- the optimal number of stages,
- the feed stream locations,
- the solvent flow rate,
- the possibility of placing intermediate streams.

The objective is to minimize the total annualized cost of equipment and utilities.

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Superstructure

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Multiple Independent Extractors

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Multiple Interconnected Extractors

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The selection of the stages in the optimal extraction cascade will be performed using the following “stage existence disjunction”.

For existing stages:

- i) Total and individual mass transfer balances.
- ii) Nonlinear equilibrium equations.
- iii) Relation between total and individual flowrates (bilinear terms).

For non-existing stages the equations considered are simply input-output relations in which no mass transfer takes place (inlet and outlet flows are the same for each phases).

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$$\left[\begin{array}{c} Z_j \\ \text{Equilibrium : } \Psi(y_{j,c}, x_{j,c}) = 0 \\ \text{Bilinear terms : } F_{j,c} = F_j \cdot u_{j,c} \end{array} \right] \vee \left[\begin{array}{c} -Z_j \\ x_{j,c} = x_{j-1,c} ; y_{j,c} = y_{j+1,c} \\ E_j = E_{j+1,c} ; E_{j,c} = E_{j+1,c} \\ R_j = R_{j-1,c} ; R_{j,c} = R_{j-1,c} \\ RL_{k,j} = 0 ; RL_{k,j,c} = 0 \\ PL_{q,j} = 0 ; PL_{q,j,c} = 0 \\ EL_j = 0 ; EL_{j,c} = 0 \end{array} \right] \quad \begin{array}{l} \forall j \in \text{NT} \\ \forall c \in \text{COMP} \\ \forall k \in \text{K} \\ \forall q \in \text{Q} \\ \forall F \in \{\text{R, E, PL}_q, \\ \text{RL}_k, \text{EL, R}_{\text{def}}\} \\ u = \{\text{x or y}\} \end{array}$$

Z_j is a boolean variable which can be true or false depending if the stage j is selected or not.

To avoid equivalent solutions that are due to the multiplicity of representation for a given number of trays, the following logic constraints are added:

$$Z_j \Rightarrow Z_{j-1} \quad \forall j \in \text{NINT}$$

Therefore, the constraints are given by the following set of equations.

- Purity and recovery requirements in the final products streams E_1 and R_{def} :

$$\left. \begin{array}{l} E_{1,kc'} \geq \xi_{E1,kc'} \cdot \left(R_{o,kc'} + \sum_{k=1}^K RL_{k,o,kc'} \right) \\ x_{Rdef,kc'} \leq \tau_{Rdef,kc'} \end{array} \right\} \text{if } kc' = \text{key component in the extract stream}$$

$$\left. \begin{array}{l} E_{1,kc''} \leq \xi_{E1,kc''} \cdot \left(R_{o,kc''} + \sum_{k=1}^K RL_{k,o,kc''} \right) \\ x_{Rdef,kc''} \geq \tau_{Rdef,kc''} \end{array} \right\} \text{if } kc'' = \text{key component in the raffinate stream}$$

- Purity and recovery requirements in the side products streams PL_q :

$$\left. \begin{array}{l} PL_{q,kc''} \geq \xi_{PLq,kc''} \cdot \left(R_{o,kc''} + \sum_{k=1}^K RL_{k,o,kc''} \right) \\ x_{PLq,kc''} \geq \tau_{PLq,kc''} \end{array} \right\} \text{if } kc'' = \text{key component in the raffinate stream}$$

• Global mass balance:

$$E_{1,c} + R_{\text{def},c} + \sum_{q=1}^Q PL_{q,c} = R_{0,c} + \sum_{k=1}^K RL_{k,c} + \sum_{j=1}^n EL_{j,c}$$

$\forall c \in \text{COMP}$

• Mass balances in each stage:

$$R_{j,c} + E_{j,c} + \sum_{q=1}^Q PL_{q,j,c} = R_{j-1,c} + E_{j+1,c} + \sum_{k=1}^K RL_{k,j,c} + EL_{j,c}$$

$\forall j \in \text{NT} \forall c \in \text{COMP}$

• Bypass mass balance:

$$R_{0,c} = R_{0,\text{ext},c} + R_{0,\text{byp},c}$$

$\forall c \in \text{COMP}$

$$R_{\text{def},c} = R_{n,c} + R_{0,\text{byp},c} + \sum_{k=1}^K RL_{k,\text{byp},c}$$

$\forall c \in \text{COMP}$

- Component and total flowrate relations (*bilinear terms*).
- Side stream balances.
- Summation mass fractions equal to 1.
- *Nonlinear* equilibrium relations.

The objective function involves the minimization of the total annualized cost of equipment and utilities. For simplicity, the total capital cost is considered proportional to the sum of stages, and the operating cost of the process, a function of the flowrate of the solvent feed stream

$$\min \quad \text{OF} = (E_0 + \sum_{j=1}^n EL_j) \cdot C_E + \sum_{j=1}^n Z_j \cdot C_n$$

Tie line Correlation Model (Reyes et al., 1999)

$$\log\left(\frac{y'_k}{y'_p}\right) = \left\{ \left[a_{k,p} + b_{k,p} \cdot \left(\frac{x'_4}{x'_2}\right) + c_{k,p} \cdot \left(\frac{x'_4}{x'_2}\right)^2 \right] + \left[d_{k,p} + e_{k,p} \cdot \left(\frac{x'_4}{x'_2}\right) + f_{k,p} \cdot \left(\frac{x'_4}{x'_2}\right)^2 \right] \cdot \log\left(\frac{x'_2}{x'_1}\right) + \left[g_{k,p} + h_{k,p} \cdot \left(\frac{x'_4}{x'_2}\right) + i_{k,p} \cdot \left(\frac{x'_4}{x'_2}\right)^2 \right] \cdot \left[\log\left(\frac{x'_2}{x'_1}\right) \right]^2 \right\}$$

$$\log\left(\frac{y'(3)}{y'(2)}\right) = k_1 \quad \log\left(\frac{y'(2)}{y'(1)}\right) = k_2 \quad \log\left(\frac{y'(4)}{y'(3)}\right) = k_3$$

$$y'(1) + y'(2) + y'(3) + y'(4) = 1 + 4 \cdot C$$

Note that: $y'(i) = y(i) + C$

Four equations with four variables !!

$$\log\left(\frac{y'(3)}{y'(2)}\right) = \left[a + b \cdot \left(\frac{x'(4)}{x'(2)}\right) + c \cdot \left(\frac{x'(4)}{x'(2)}\right)^2 \right] + \left[d + e \cdot \left(\frac{x'(4)}{x'(2)}\right) + f \cdot \left(\frac{x'(4)}{x'(2)}\right)^2 \right] \cdot \log\left(\frac{x'(2)}{x'(1)}\right) + \left[g + h \cdot \left(\frac{x'(4)}{x'(2)}\right) + i \cdot \left(\frac{x'(4)}{x'(2)}\right)^2 \right] \cdot \left[\log\left(\frac{x'(2)}{x'(1)}\right) \right]^2$$

$$\log\left(\frac{y'(2)}{y'(1)}\right) = \left[a' + b' \cdot \left(\frac{x'(4)}{x'(2)}\right) + c' \cdot \left(\frac{x'(4)}{x'(2)}\right)^2 \right] + \left[d' + e' \cdot \left(\frac{x'(4)}{x'(2)}\right) + f' \cdot \left(\frac{x'(4)}{x'(2)}\right)^2 \right] \cdot \log\left(\frac{x'(2)}{x'(1)}\right) + \left[g' + h' \cdot \left(\frac{x'(4)}{x'(2)}\right) + i' \cdot \left(\frac{x'(4)}{x'(2)}\right)^2 \right] \cdot \left[\log\left(\frac{x'(2)}{x'(1)}\right) \right]^2$$

$$\log\left(\frac{y'(4)}{y'(3)}\right) = \left[a'' + b'' \cdot \left(\frac{x'(4)}{x'(2)}\right) + c'' \cdot \left(\frac{x'(4)}{x'(2)}\right)^2 \right] + \left[d'' + e'' \cdot \left(\frac{x'(4)}{x'(2)}\right) + f'' \cdot \left(\frac{x'(4)}{x'(2)}\right)^2 \right] \cdot \log\left(\frac{x'(2)}{x'(1)}\right) + \left[g'' + h'' \cdot \left(\frac{x'(4)}{x'(2)}\right) + i'' \cdot \left(\frac{x'(4)}{x'(2)}\right)^2 \right] \cdot \left[\log\left(\frac{x'(2)}{x'(1)}\right) \right]^2$$

Tie Lines Correlation

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Solubility Surface Correlation Model

$$x'(3) + x'(4) = (A' \cdot M + B') \cdot (x'(1) + x'(4)) + (C' \cdot M + D')$$

$$x'(2) + x'(4) = (A \cdot M^2 + B \cdot M + C) \cdot (x'(1) + x'(4))^2 + (D \cdot M^2 + E \cdot M + F) \cdot (x'(1) + x'(4)) + (G \cdot M^2 + H \cdot M + I)$$

$$M = \frac{x'(4)}{x'(4) + x'(2)}$$

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Solubility Surface Correlation

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First approach: MINLP techniques.

- i. Formulating all equations using big-M inequalities
- ii. DICOPT (GAMS)

Difficulties: **VERY SENSITIVE TO:**

- i. INITIAL POINT (Local Optimums, Infeasible)
- ii. MILP SOLVER USED (OSL, MINOS, CPLEX...)

**GENERAL
DISJUNCTIVE
PROGRAMMING**

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GENERAL DISJUNCTIVE PROGRAMMING ALGORITHM

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Big M formulation

Linear constraints

$$\begin{bmatrix} Z_j \\ G(t) = H(t') \end{bmatrix} \vee \begin{bmatrix} -Z_j \\ G(t) = S(t') \end{bmatrix} \Rightarrow \begin{cases} -M_H \cdot (1 - Z_j) + H(t') \leq G(t) \leq M_H \cdot (1 - Z_j) + H(t') \\ -M_S \cdot Z_j + S(t') \leq G(t) \leq M_S \cdot Z_j + S(t') \end{cases}$$

For instance:

$$\left. \begin{aligned} R_{j-1} - M_R \cdot (1 - Z_j) &\leq R_j \leq R_{j-1} + M_R \cdot (1 - Z_j) \\ E_{j+1} - M_E \cdot (1 - Z_j) &\leq E_j \leq E_{j+1} + M_E \cdot (1 - Z_j) \end{aligned} \right\} \quad \forall j \in NT$$

Constraints with linear approximations

slack variables are introduced to make mathematically feasible all the different linearizations of the same nonlinear and nonconvex equation P in the different points corresponding to the previous NLP solutions.

$$\left. \begin{aligned} P_s(\bar{u}^{nl}) + \nabla P_s(\bar{u}^{nl}) \cdot (\bar{u} - \bar{u}^{nl}) &\leq M_{P_s} \cdot (1 - Z_j) + sv1(P_s^{nl}) \\ P_s(\bar{u}^{nl}) + \nabla P_s(\bar{u}^{nl}) \cdot (\bar{u} - \bar{u}^{nl}) + sv2(P_s^{nl}) &\geq -M_{P_s} \cdot (1 - Z_j) \end{aligned} \right\} \quad \forall s \in NLF, \forall nl \in PNLP$$

$$\left. \begin{aligned} P_s(\bar{u}^{nl}) + \nabla P_s(\bar{u}^{nl}) \cdot (\bar{u} - \bar{u}^{nl}) &\leq M_{P_s} \cdot (1 - Z_j) \end{aligned} \right\} \quad \forall j \in NT, \forall c \in COMP$$

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Simple extractor.

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Evolution of the annual cost and solvent flowrate vs. number of stages for example 1.

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Extractor with 1 side feed stream.

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Extractor with 1 side product stream.

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2 independent extractors.

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2 interrelated extractors.

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Characteristics of the initial GDP model for the different examples.

	Example:	1	2	3	4	5
<i>NLP</i>	No equations	503	547	547	953	2116
<i>Subproblem</i>	No. cont. var.	300	350	350	586	866
	CPU time (s)	1.3	2.5	8.3	10	49
<i>MILP</i>	No of equations	1130	1317	1317	4113	6124
<i>master</i>	No. cont. var.	2950	3800	3800	11000	19196
<i>problem</i>	No. boolean var.	10	10	10	20	10
	CPU time (s)	69.6	69	80.3	3301	443
<i>Total</i>	CPU time (s)	71	71.5	88.6	1110	492
<i>Total</i>	loops	6	5	4	12	7

The major bottleneck is the solution of the MILP master problem, due to the presence of binary variables.

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Future work:

Possibility of including distillations columns in order to recover the extraction solvent

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1 feed stream, 2 extractor with multiple solvent feeds and using 2 different solvents in each extractor.

Global Optimization:

- Good Bounds
- Convex underestimators
- Spatial Branch and Bound

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• Component and total flowrate relations (*bilinear terms*).

$$\left. \begin{array}{ll} R_{j,c} - R_j x_{j,c} = 0 & E_{j,c} - E_j y_{j,c} = 0 \\ EL_{j,c} - EL_j y_{EL,j,c} = 0 & RL_{k,j,c} - RL_{k,j} x_{RL,k,c} = 0 \\ PL_{q,j,c} - PL_{q,j} x_{j,c} = 0 & \end{array} \right\} \begin{array}{l} \forall j \in NT, \forall c \in COMP \\ \forall k \in K, \forall q \in Q \end{array}$$

$$\left. \begin{array}{ll} R_{def,c} - R_{def} x_{def,c} = 0 & R_{0,byp,c} - R_{0,byp} x_{0,c} = 0 \\ R_{0,ext,c} - R_{0,ext} x_{0,c} = 0 & RL_{k,byp,c} - RL_{k,byp} x_{RL,k,c} = 0 \\ PL_{q,c} - PL_q x_{PL,q,c} = 0 & \end{array} \right\} \begin{array}{l} \forall c \in COMP \\ \forall k \in K, \forall q \in Q \end{array}$$

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OPTIMAL SYNTHESIS OF LIQUID-LIQUID MULTISTAGE EXTRACTORS using Generalized Disjunctive Programming (GDP)

• COMPLEX EXTRACTOR DESIGN (GDP)

<http://newton.cheme.cmu.edu/interfaces/extractor/main.html>

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