Chemical product centric sustainable process design: Targeted reverse process design & concept of process group based flowsheet synthesis

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Targeted reverse process design & concept of process group based flowsheet synthesis:

- **Solvent-based environmentally acceptable process design**
- Driving force based separation process design
- Process group based flowsheet synthesis
We have an aqueous mixture of phenol in a waste water stream. We need to remove the phenol. Benzene is known as a solvent but due to environmental reasons, we cannot use it. What should be a good replacement solvent for benzene?
Determine target for solvent

* \( f_s = F_w (X_{in,s} - X_{out,s}) \)

Solubility, \( S = \frac{f_s}{F_s} \)

* Find solvent to match target \( S \) – use data & models

Problem solution

* \( f_s = 100 \ (0.018 - 0.00) \)

Solubility, \( S = \frac{1.8}{F_s} \)

• Solvent ID provides \( S \)
• \( F_s = S/1.8 \)
• Solvent ID decides extraction process; solvent-solute relations identify the process parameters

Order different solutions according to cost of solvent & operation
Define target (substitute benzene)

* Property specifications:
  – $T_b > 322 \text{ K}$
  – $T_m < 314 \text{ K}$
  – $29 \text{ kJ/mol} < H_{vap} < 34 \text{ kJ/mol}$
  – $\log P > 1.5$
  – High solvent power
  – High Phenol precipitation mole fraction at 298 K
Match target: Initial search (generate candidates)

* Property specifications (revised target):
  - $T_b > 322$ K
  - $T_m < 314$ K
  - $\delta_{SP}$

* Use the above properties to search among non-aromatic compounds

* Design acyclic compounds: alcohols, ketones, aldehydes, ethers.
Solvent substitution in process design

Match target through CAMD – reverse design

Chemical product centric sustainable process design - Lecture 3
Solvent substitution in process design

- **Product-process evaluation**
  - High precipitation mole fractions of phenol.
  - A CAS Registry number exists (availability & additional information)

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>LogP = 1.56</td>
<td>LogP = 1.63</td>
</tr>
<tr>
<td>Phenol molefraction = 0.759</td>
<td>Phenol molefraction = 0.785</td>
</tr>
<tr>
<td>Methyl sec-Butyl Ether</td>
<td>2,2-Dimethyl-1-propanal</td>
</tr>
<tr>
<td>CASNO: 6795-87-5</td>
<td>CASNO: 630-19-3</td>
</tr>
</tbody>
</table>
Solvent substitution in process design

Process evaluation

SLE Diagram for Phenol/Solvent system

- Benzene (experimental $T_{\text{fusion}}$)
- Benzene (estimated $T_{\text{fusion}}$)
- Methyl sec-Butyl Ether (estimated $T_{\text{fusion}}$)
Example: Separation of an azeotropic mixture

Problem: A process stream of 50 mole% Acetone and 50 mole% Chloroform at 300K, is to be separated.

No external medium known; Binary ratios of properties identify the following alternatives:

Separation techniques considered:
- Adsorption (liquid, gas)
- Crystallization
- Desublimation
- Distillation – simple
- Distillation – extractive
- Distillation with decanter
- Liquid-liquid extraction
- Flash/evaporation
- Membrane (gas, liquid)
- Microfiltration
- Partial condensation

Separation techniques:
- Distillation – simple
- Distillation – extractive
- Distillation – azeotropic
- Liquid extraction
- Pressure swing

Note: Acetone-chloroform forms a high boiling azeotrope that is slightly pressure sensitive.
Solvent design sub-problem

- CAMD problem:
  - $340 < T_{\text{boil}} < 420$
  - Selectivity $> 3.5$
  - Solvent power $> 2.0$
  - No azeotropes

Solution:
- 1-Hexanal
- Methyl-n-pentyl ether (Benzene)

- Number of compounds designed: 47792
- Number of compounds selected: 53
- Number of isomers designed: 528
- Number of isomer selected: 23
- Total time used to design: 57.01 s
Summary: CAMD-based solvent selection

- Solvent selection/design based on CAMD is very large but application is limited by availability of suitable property models (separation, reactions, formulated products, ...)
- Extension to solvent mixture (blend) design is simple and easy
- Integration of process and product design is possible (requires methods & tools integration)
- Available software: ICAS-ProCAMD
Targeted reverse process design & concept of process group based flowsheet synthesis:

- Solvent-based environmentally acceptable process design
- **Driving force based separation process design**
- Process group based flowsheet synthesis
• Sustainable process (design) alternatives can be generated by targeting designs that utilize the maximum available driving force

• Use of maximum driving force implies minimum corresponding energy, and therefore, improved sustainability
Definition of driving force

Separation of compound $i$ from compound $j$

\[ y_i = x_i \alpha_{ij} / (1 + x_i (\alpha_{ij} - 1)) \]

\[ F_{Di} = y_i - x_i \]
\[ = x_i \beta_{ij} / (1 + x_i (\beta_{ij} - 1)) \]
\[ - x_i \]
\[ \beta_{ij} = f(T, P, x, y, \phi) \]

Energy or work needed to perform an operation is inversely proportional to the driving force
Definition of Driving Force - $D_{ij}$

Separation of compound $i$ from compound $j$

$$y_i = \frac{x_i \alpha_{ij}}{1 + x_i (\alpha_{ij} - 1)}$$

$$D_{ij} = y_i - x_i$$

$$= \frac{x_i \beta_{ij}}{1 + x_i (\beta_{ij} - 1)}$$

$$- x_i$$

$$\beta_{ij} = f(T, P, x, y, \phi)$$

$D_{ij}$ for 4 types vapor-liquid separation range

Theory: $D_{ij}$ is inversely proportional to energy consumption and directly proportional to separability.
Example: VLE based separation using $D_{ij}$

**Typical 2-Phase VLE-Model**

**Equilibrium condition**

$$y_i = \frac{x_i \alpha_{ij}}{[x_i (\alpha_{ij} - 1) + 1]} \quad \text{w.r.t. relative volatility}$$

**Equilibrium condition**

$$D_{ij} = \frac{x_i \alpha_{ij}}{[x_i (\alpha_{ij} - 1) + 1]} - x_i \quad \text{w.r.t. driving force}$$

**Mass Balance**

$$Z \ z_i = V \ y_i + L \ x_i$$

or

$$y_i = (R + 1) \ z_i - R \ x_i$$

or

$$D_{ij} = (R + 1) \ (z_i - x_i)$$

where $R = L/V$
\[ D_{ij} = y_{ij} - x_{ij} = x_{ij} \alpha_{ij} / (1 + x_{ij} (\alpha_{ij} - 1)) - x_{ij} \]

Example: VLE based separation using \( D_{ij} \)

When \( D_{ij} = 0 \), there is no separation and \( z_{i} = x_{i} \)

When \( L = 0 \) or \( V = \infty \), \( R = L/V = 0 \), \( D_{ij} = z_{i} - x_{i} \)

When \( x_{i} = 0 \), \( D_{ij} = (R + 1) z_{i} \)
Separation of Binary Mixtures by Distillation

Component Mass Balance

Overall

\[ F \, z^F = D \, x^D + B \, x^B \]

Rectifying section

\[ y_{n+1} = \frac{L_n}{V_{n+1}} \, x_n + \frac{D}{V_{n+1}} x^D \]

\[ y = \left[ \frac{R}{(R+1)} \right] x + \left[ \frac{1}{(R+1)} \right] x^D \]

Stripping section

\[ y_{m+1} = \frac{L_m}{V_{m+1}} \, x_m - \frac{B}{V_{m+1}} x^B \]

\[ y = \left[ \frac{(V_B+1)}{V_B} \right] x - \frac{1}{(V_B+1)} x^B \]

Equilibrium relation

\[ y_i = x_i \, \alpha_{ij} / (1 + x_i \, (\alpha_{ij} - 1)) \]
Equilibrium relation

\[ y_i = x_i \alpha_{ij} / (1 + x_i (\alpha_{ij} - 1)) \]

Component Mass Balance

Overall

\[ F \ z^F = D \ x^D + B \ x^B \]

Rectifying section

\[ y_{n+1} = \frac{L_n}{V_{n+1}} \ x_n + \frac{D}{V_{n+1}} x^D \]

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Stripping section

\[ y_{m+1} = \frac{L_m}{V_{m+1}} \ x_m - \frac{B}{V_{m+1}} x^B \]

\[ y = \left[ \frac{(V_B+1)}{V_B} \right] x - \left[ \frac{1}{(V_B+1)} \right] x^B \]
Given a mixture to be separated into two products in a distillation column with $N$ trays. What is the optimal (w.r.t the costs of operation) feed plate location and the corresponding reflux ratio for different product purity specifications?

\[ \text{Driving force versus reverse design} \]

\[ N_F = N(1-D_x) \]
Max $F_{Di} \equiv \frac{d(D_{ij})}{dx_i} = 0 = \frac{d( x_i \alpha_{ij} / (1 + x_i (\alpha_{ij} - 1)))}{dx_i} - 1$

Every $\alpha_{ij}$ has a corresponding $D_{ij}(\text{max})$ & $x_i(\text{max})$, which has a corresponding NP, NF, $xD_i$, $xB_i$
## Identification of design targets

<table>
<thead>
<tr>
<th>$F_{D,\text{Max}}$</th>
<th>$X_{i,\text{Max}}$</th>
<th>Limit $X_{\text{Feed}}$</th>
<th>$X_{\text{LK,Min}}$</th>
<th>$X_{\text{LK,Bet}}$</th>
<th>RR$_{\text{Min}}$</th>
<th>C</th>
<th>RR$_{\text{Min}}$ + C</th>
<th>N$_{\text{ideal}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.065</td>
<td>0.45</td>
<td>0.2 ≤ $X_{F,\text{LK}}$ ≤ 0.8</td>
<td>0.995</td>
<td>0.005</td>
<td>9.89</td>
<td>1.5</td>
<td>14.83</td>
<td>96</td>
</tr>
<tr>
<td>0.101</td>
<td>0.44</td>
<td>0.2 ≤ $X_{F,\text{LK}}$ ≤ 0.8</td>
<td>0.995</td>
<td>0.005</td>
<td>9.89</td>
<td>1.5</td>
<td>14.36</td>
<td>71</td>
</tr>
<tr>
<td>0.146</td>
<td>0.42</td>
<td>0.2 ≤ $X_{F,\text{LK}}$ ≤ 0.8</td>
<td>0.995</td>
<td>0.005</td>
<td>9.89</td>
<td>1.5</td>
<td>13.33</td>
<td>54</td>
</tr>
<tr>
<td>0.195</td>
<td>0.02</td>
<td>7.33</td>
<td>1.5</td>
<td>11.0</td>
<td>67</td>
<td>1.5</td>
<td>12.33</td>
<td>41</td>
</tr>
<tr>
<td>0.225</td>
<td>0.05</td>
<td>7.10</td>
<td>1.5</td>
<td>10.65</td>
<td>67</td>
<td>1.5</td>
<td>11.0</td>
<td>67</td>
</tr>
<tr>
<td>0.268</td>
<td>0.10</td>
<td>6.64</td>
<td>1.5</td>
<td>9.96</td>
<td>38</td>
<td>1.5</td>
<td>10.65</td>
<td>50</td>
</tr>
<tr>
<td>0.382</td>
<td>0.05</td>
<td>6.64</td>
<td>1.5</td>
<td>8.58</td>
<td>29</td>
<td>1.5</td>
<td>10.65</td>
<td>50</td>
</tr>
<tr>
<td>0.478</td>
<td>0.02</td>
<td>6.64</td>
<td>1.5</td>
<td>8.58</td>
<td>29</td>
<td>1.5</td>
<td>10.65</td>
<td>50</td>
</tr>
</tbody>
</table>

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Chemical product centric sustainable process design - Lecture 3
1. Given a mixture to be separated by distillation

2. Select a pressure and calculate the $D_{ij}$ for all pairs of binary mixtures (ordered w.r.t. boiling point)

3. Identify the $\alpha_{ij}$ and from it, $D_{ij}$ (max), $x_i$ (max) for specific products $xD_i$ and $xB_i$

4. Use the table of $\alpha_{ij}$, $D_{ij}$ (max), $x_i$ (max), NP, NF, .... To read out the remaining design variables
Application example

Given:

Separation binary mixture of butane and i-butane; 
P = 5 atm; NP = 60

Solution:

Calculate $\alpha_{ij}$ at 5 atm = 1.33

From Figure, obtain $D_{ij} \text{(max)} = 0.074; x_i \text{(max)} = 0.45$

Select $X_{B, HK} = 0.995 \& X_{D, LK} = 0.995$

NF = 60 (1 - 0.45) = 33

From Table, find $RR_{\min} = 6.4$
Specify: top and bottom compositions.
Determine: Dx (NF), Ds (NS) and RRmin.
\[ N_S = N(1-Ds) \]
\[ N_F = N(1-Dx) \]

Driving force based design – Complex columns

- \( N_S \): The relative position of the side-draw
- \( Ds \): Position of the feed stream
- \( Dx \): The relative position of the feed stream
Order the driving force diagrams in terms of $f_{ij|_{\text{max}}}$; configure the distillation train in terms of $f_{ij|_{\text{max}}}$; design each distillation column in terms of intersection on $D_yD_x$ line.
Hybrid Separation: Driving force

Separation by single distillation operation not feasible; hybrid separation schemes (solvent based extraction or distillation plus pervaporation or pressure swing distillation) feasible
Hybrid Separation: Optimal design

Distillation plus pervaporation requires 34.5 % less energy if the product from the first distillation = 62% MTBE. Distillation columns in both schemes optimized in terms of intersection of operating lines.
Targeted reverse process design & concept of process group based flowsheet synthesis:

• Driving force based separation process design
• Solvent-based environmentally acceptable process design
• Process group based flowsheet synthesis
Process groups based flowsheet synthesis

CAMD
Given a set of target properties, find the molecules or mixture that match the target properties
A set of building blocks: CH₂, C≡C, CH₃OH, HCOO,...
Set of property based numerical constraints

CAFD
Given a multicomponent mixture, separate into a pure product streams
A set of building blocks: (A/BC), (AB/CD), (cyc G/H)...
Set of property based numerical constraints

Definition problem
Translation into mathematical problem
Generation of alternatives & optimal design
Post synthesis-design analysis

Simultaneous product-process design
Group contribution approach for synthesis/design of molecules as well as process flowsheets
Atomic-groups are used to design molecules while process-groups are used to design flowsheets

L. d’Anterroches, et al. 2005
Idea of GC Based Process Property Model

We need process groups (PG) to represent the process flowsheet

- A process-group ensures a satisfied mass-balance
- Connectivity is component, P and T dependent

L. d’Anterroches, PhD-Thesis, 2005
Idea of GC Based Process Property Model

We need PGs to represent the process flowsheet

Production of methyl acetate
Extension of the GC-approach to Process Design

Idea of GC Based Process Property Model

We need PGs to represent the process flowsheet

- Reactor: Kinetics (rBD/pABCD)
- Distillation: Driving force (ABC/CD)
- Molecular sieve size (ms AB/C)
- Pressure Swing: Azeotrope pressure dependent (sw A/B)
- Distillation + Pervaporation: Driving force, solubility parameter, ...

Diagram showing the relationships between these components.
We need PG parameter tables & GC-based property model!

- Energy index for distillation column process-group

\[
E_x = \sum_{k=1}^{n=NG} Q_k = \sum_{k=1}^{n=NG} \left( \frac{1 + p_k}{d_{ij}^k} \times a_k + A \right)
\]

- \(p_k\): Topology factor
- \(a_k\): Regressed contribution of PG \(k\)
- \(d_{ij}^k\): Driving force between the 2 key components
- \(A\): Regressed constant

Also, similar models for reactors; solvent-based extraction; membrane-based separation has been developed

L. d’Anterroches, PhD-Thesis, 2005
Integration of product-process design

Simultaneous product-process design

Groups to represent operations

Table 1: List of currently available process-groups (PG)

<table>
<thead>
<tr>
<th>Operation</th>
<th>Examples of Process-Groups</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distillation column</td>
<td>(A/BC), (ABC/DE)</td>
</tr>
<tr>
<td>Solvent based azeotropic distillation</td>
<td>(cycA/B)</td>
</tr>
<tr>
<td>Flash separation</td>
<td>(fABC/BCD)</td>
</tr>
<tr>
<td>Kinetic-model based reactor</td>
<td>(rABC/nE/pABC)</td>
</tr>
<tr>
<td>Fixed conversion reactor</td>
<td>(rABC/nE/pABCD)</td>
</tr>
<tr>
<td>Pressure swing distillation</td>
<td>(swA/B)</td>
</tr>
<tr>
<td>Polar molecular sieve based separation</td>
<td>(pmsABC/D)</td>
</tr>
<tr>
<td>Molecular sieve based separation</td>
<td>(msABC/D)</td>
</tr>
<tr>
<td>Liquid membrane based separation</td>
<td>(lmemABC/D)</td>
</tr>
<tr>
<td>Gas membrane based separation</td>
<td>(gmemABC/D)</td>
</tr>
<tr>
<td>Crystallization</td>
<td>(crsABC/D)</td>
</tr>
<tr>
<td>Adsorption</td>
<td>(abEAB/eF/EABF/EF)</td>
</tr>
</tbody>
</table>

Method to represent flowsheets
Algorithm for flowsheet structures generation
Evaluation of flowsheets: Property model

L. d’Anterroches, PhD-Thesis, 2005
Case Study: Distillation Sequence

An example from literature
General notation system

Representation of molecule, process flowsheet or operations & reaction networks with SMILES & SFILES

\[
\begin{align*}
(1) \quad & H_2 + l \rightleftharpoons H_2l \\
(2) \quad & H_2l + l \rightleftharpoons Hl + Hl \\
(3) \quad & N_2 + l \rightleftharpoons N_2l \\
(4) \quad & N_2l + l \rightleftharpoons Nl + Nl \\
(5) \quad & N_2l + H_2l \rightleftharpoons N_2H_2l + l \\
(6) \quad & N_2H_2l + l \rightleftharpoons NHl + NHl \\
(7) \quad & NHl + Hl \rightleftharpoons NH_2l + l \\
(8) \quad & NHl + H_2l \rightleftharpoons NH_3l + l \\
(9) \quad & NH_2l + Hl \rightleftharpoons NH_3l + l \\
(10) \quad & NH_3l \rightleftharpoons NH_3 + l \\
\end{align*}
\]

SMILES & SFILES

N#C=NC(NC)NCCSCC1NC=NCC1=C

(H2)(1)<1(H2l)2(5)4<3(1)>1<6<5[(3)[(N2l)3]<(n2)](6)[NH1](9)<2(NH3l)(11)<6(NH3)<(N2H2l)<4

(iAD)(rAD/pABCDE)<1<2(fAB/ABCDE)1[(AB/CDE)oAB])[C/DE][oC])(D/E)2(oE)
Summary: Targeted Process Design

• A systematic methodology for targeted process design matching the needs of specific products has been presented together with examples.

• Use of the concept for design of processes using solvents, processes using the maximum available driving force, & for generating and evaluating process flowsheets (CAFD) has been highlighted.