UNIVERSITY OF TWENTE.

DESIGN OF AZEOTROPIC AND EXTRACTIVE DIVIDING-WALL COLUMNS BY MINLP METHODS

WORKSHOP ON DIVIDED-WALL DISTILLATION IN TRONDHEIM, OCTOBER 5, 2023
IN THIS PRESENTATION:

MINLP OPTIMIZATION OF DWC COLUMNS
THERMODYNAMIC EFFICIENCY
EXTRACTIVE DIVIDING-WALL COLUMNS
AZEOTROPIC DIVIDING-WALL COLUMNS
For a DWC, many degrees of freedom must be fixed…
... a suitable model structure must be chosen ...

- Thermodynamic equivalent representation of DWC by 4-section column model
the model equations must be written...

- **MESH equations for** $n = 1 \ldots N_{\text{max}}$ **stages:**

  \[
  V_{n+1} x_{V_{n+1}} + L_{n-1} x_{L_{n-1}} + F_n x_{F_n} + L_{R_n} x_{L_{R_n}} + R_n x_{R_n} = V_n x_{V_n} + L_n x_{L_n} + S_n x_{S_n}
  \]

  \[x_{V_n} = K_n x_{L_n}\]

  \[
  \sum x_{V_n} = 1 \quad \text{and} \quad \sum x_{L_n} = 1
  \]

- **Mixed-integer and pure integer constraints:**

  \[
  F_n \leq F \cdot y_{F,n} \quad \text{and} \quad \sum y_{F,n} = 1
  \]

  \[
  L_{R,n} \leq L_R \cdot y_{R,n} \quad \text{and} \quad \sum y_{L_{R,n}} = 1
  \]

  \[
  R_n \leq R \cdot y_{R,n} \quad \text{and} \quad \sum y_{R,n} = 1
  \]

  \[
  S_n \leq S \cdot y_{R,n} \quad \text{and} \quad \sum y_{S,n} = 1
  \]

- **Auxiliary model equations:**

  \[N_S = \sum y_{R,n} \cdot n - \sum y_{L_{R,n}} \cdot n + 1 \quad + \text{Pressure Drop Correlations}\]
... the optimization problem must be set up

- Constraints:
  - Equality constraints (model equations) \( h \)
  - Inequality constraints (design specs) \( g \)
  - Mixed-integer constraints \( x - My \leq 0 \)
  - Pure integer constraints \( yE = e \)

- Optimization variables:
  - Continuous variables \( d \)
  - Binary (integer) variables \( y \)

- Objective function \( f(x,y) \):
  - \( f(x,y) = \text{Total Annual Costs (TAC)} \)
  - \( TAC = C_{op} + 5 \times C_{eqp} \times 0.2 \)

\[
Z = \min_{d,y} f(x,y)
\]

subject to
\[
\begin{align*}
  h(x,y) &= 0 \\
  g(x,y) &\leq 0 \\
  x - My &\leq 0 \\
  yE &= e \\
  x &\in \mathbb{R}^{nx}, y \in \{0,1\}^{ny}
\end{align*}
\]

Remark:
\( d \) is the vector of optimization variables and a subset of all cont. \( x \)
... with special attention to DWC equipment costs ... 

- Equipment costs of DWC consists of 4 pressure vessels with internals plus condenser and reboiler:

\[ C_{eqp} = C_{eqp,D-1} + C_{eqp,D-2} + C_{eqp,D-3} + C_{eqp,D-4} + C_{eqp,Cond} + C_{eqp,Reb} \]

- Overestimation of DWC equipment costs, but consistent with model structure, easy to implement, and for comparative studies (probably) sufficient
... and finally, the problem must be solved.

Selection of continuous (operating) variables

Selection of binary (design) variables

Start

NLP Subproblem

Aspen+, ACM, ...

MILP Master Problem

Excel, Python, ...

(Solution)

Outer Iteration Loop (Flowsheet optimization variables)

Inner Iteration Loop (Integer and cont. unit optimization variables)


Relative TAC

# Iterations

0,9 1,0 1,1 1,2 1,3

1 2 3 4 5

NLP

MILP

04.10.2023 Design of Azeotropic and Extractive DWC
Thermodynamic Efficiency of DWC

2-Column-Sequence

DWC

Back mixing (= twofold separation = inefficiency)
MINLP Results for a Very Prominent Example

<table>
<thead>
<tr>
<th></th>
<th>D-1</th>
<th>D-2</th>
<th>DS</th>
<th>DWC</th>
<th>Sav.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q / MW</td>
<td>24.9</td>
<td>24.6</td>
<td>49.5</td>
<td>35.6</td>
<td>28%</td>
</tr>
<tr>
<td>No. of stages</td>
<td>28</td>
<td>22</td>
<td>50</td>
<td>49</td>
<td>2%</td>
</tr>
<tr>
<td>Rel. OpEx</td>
<td>0.37</td>
<td>0.36</td>
<td>0.73</td>
<td>0.53</td>
<td>27%</td>
</tr>
<tr>
<td>Rel. CapEx</td>
<td>0.13</td>
<td>0.14</td>
<td>0.27</td>
<td>0.22</td>
<td>19%</td>
</tr>
<tr>
<td>Rel. TAC</td>
<td>0.5</td>
<td>0.5</td>
<td>1</td>
<td>0.75</td>
<td>25%</td>
</tr>
</tbody>
</table>

Thermodynamic Efficiency of DWC

Twofold separation = inefficiency
Derivation of Extractive Dividing-Wall Column

Extractive Distillation

Entrainer E

A + B

D-1

D-2

A

B

Extractive Distillation w/ Side Rectifier

Entrainer E

A + B

D-1

D-2

A

B

Extractive Dividing-Wall Column (Ledge Wall)

Entrainer E

A + B

A

B

Kiss, Suszwala (2015): Enhanced bioethanol dehydration by extractive and azeotropic distillation in DWC
Czarnecki et al. (2023): Extractive Dividing Wall Column for Separating Azeotropic Systems: A Review
Extractive DWC: 3-Column Substitution Model
Extractive Distillation in a Dividing-Wall Column (EDWC)

*Flowsheet optimization variables

<table>
<thead>
<tr>
<th></th>
<th>D-1</th>
<th>D-2</th>
<th>ED</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q / kJ/kg EtOH</td>
<td>1401</td>
<td>188</td>
<td>1589</td>
</tr>
<tr>
<td>No. of stages</td>
<td>39</td>
<td>14</td>
<td>53</td>
</tr>
<tr>
<td>Rel. OpEx</td>
<td>0.71</td>
<td>0.1</td>
<td>0.81</td>
</tr>
<tr>
<td>Rel. CapEx</td>
<td>0.16</td>
<td>0.03</td>
<td>0.19</td>
</tr>
<tr>
<td>Relative TAC</td>
<td>0.87</td>
<td>0.13</td>
<td>1.00</td>
</tr>
</tbody>
</table>

EtOH (0.999)
H2O (0.999)

$E^* = 0.69 \cdot F$
$x_{EG}^* = 0.99997$

$R_R = 0.4$
$R_R = 0.6$

$F = 0.88$

$D-1$
$D-2$

$p = 1 \text{ bar}$
$p = 0.26 \text{ bar}$

155 °C

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Design of Azeotropic and Extractive DWC
Extractive Distillation in a Dividing-Wall Column (EDWC)

<table>
<thead>
<tr>
<th></th>
<th>D-1</th>
<th>D-2</th>
<th>ED</th>
<th>EDWC</th>
<th>Sav.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q / kJ/kg EtOH</td>
<td>1401</td>
<td>188</td>
<td>1589</td>
<td>1664</td>
<td>-5%</td>
</tr>
<tr>
<td>No. of stages</td>
<td>39</td>
<td>14</td>
<td>53</td>
<td>42</td>
<td>21%</td>
</tr>
<tr>
<td>Rel. OpEx</td>
<td>0.71</td>
<td>0.1</td>
<td>0.81</td>
<td>0.94</td>
<td>-16%</td>
</tr>
<tr>
<td>Rel. CapEx</td>
<td>0.16</td>
<td>0.03</td>
<td>0.19</td>
<td>0.2</td>
<td>-5%</td>
</tr>
<tr>
<td>Relative TAC</td>
<td>0.87</td>
<td>0.13</td>
<td>1</td>
<td>1.14</td>
<td>-14%</td>
</tr>
</tbody>
</table>
Although double separation is avoided, the extractive dividing-wall column is **not** a viable option for separating near-azeotropic ethanol/water mixtures because the pressures cannot be selected independently.
For low-purity specifications of water stream, side-stream columns can be a viable option.

Derivation of Azeotropic Dividing-Wall Column

Heteroazeotropic Distillation

Heteroazeotropic Distillation /w Side Stripper

Heteroazeotropic Dividing-Wall Column

Examples:
Sun et al. (2011): Implementation of Ethanol Dehydration Using Dividing-Wall Heterogeneous Azeotropic Distillation Column
Le, Halvorsen, Pajalic, Skogestad (2015): Dividing wall columns for heterogeneous azeotropic distillation
Azeotropic Distillation: 3-Column Substitution Model
Azeotropic Dividing-Wall Column (ADWC)

The ADWC is an economically attractive option for separating near-azeotropic ethanol/water mixtures.

<table>
<thead>
<tr>
<th>*Flowsheet Optimization Variables</th>
<th>D-1</th>
<th>D-2</th>
<th>AD</th>
<th>ADWC</th>
<th>Sav.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q / kJ/kg EtOH</td>
<td>2020</td>
<td>1483</td>
<td>3503</td>
<td>3197</td>
<td>9%</td>
</tr>
<tr>
<td>No. of stages</td>
<td>97</td>
<td>23</td>
<td>120</td>
<td>60</td>
<td>50%</td>
</tr>
<tr>
<td>Rel. OpEx</td>
<td>0.38</td>
<td>0.28</td>
<td>0.66</td>
<td>0.59</td>
<td>11%</td>
</tr>
<tr>
<td>Rel. CapEx</td>
<td>0.25</td>
<td>0.09</td>
<td>0.34</td>
<td>0.29</td>
<td>15%</td>
</tr>
<tr>
<td>Rel. TAC</td>
<td>0.63</td>
<td>0.37</td>
<td>1</td>
<td>0.88</td>
<td>12%</td>
</tr>
</tbody>
</table>
Conventional Sequence vs. Dividing-Wall Column

$p = 1$ atm
Why does the ADWC perform better?

For comparison, number of stages has been set to 99.
Why does the ADWC perform better? – cont’d

Feed: 15th stage

Dividing-Wall Section (# 35 - # 58)

Water profile of conventional column
Why does the ADWC perform better? – cont’d

The diagram illustrates the liquid-phase concentration for different components over the number of stages. The x-axis represents the number of stages, while the y-axis shows the liquid-phase concentration in mol/mol.

- **Cyclohexane profile of conventional column**
- **Water profile of conventional column**

The graph shows that the ADWC performs better in terms of separation efficiency, as indicated by the concentration profiles for different components.
DWC Gives Rise to Alternative Designs

![Diagram of DWC process](image)

04.10.2023

Design of Azeotropic and Extractive DWC
Conclusions

• DWC is not always the best choice
• Fair (optimization-based) comparison needed
• Visual inspection of concentration profiles not sufficient
• Pressure is an important (but often neglected) optimization variable (degree of freedom)