Continuous processes – sustainable manufacturing
Chlorination, sulfonation and methylation at CABB

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Continuous processes - Sustainable manufacturing

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Summary
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Continuous Flow Technology

- Association with microreactors, process intensification and "smaller" reaction volumes
- Advantages of safety (hazardous reactions, pressurisation, heat exchange), scalability and automation
- Continuous processes were identified as most important topic for green manufacturing

Sustainability

- Green chemistry – sustainable chemistry
- Efficient, safe and environmentally benign chemical products and processes
- Protecting and enhancing human health and the environment
- Reducing the environmental impact of processes and products, minimising waste
- Extending the quality of life; competitive, knowledge-based, enterprise-led economy

CABB

- Chlorination, sulfonation, methylation
- Long history in continuous processes; dedicated and multi-purpose continuous plants
- Series of continuous standard unit operations
- Sustainability by combining continuous processes with Verbund and recycling system

1 Org. Process Res. Dev, DOI: 10.1021/op100327d
12 Principles of Green Chemistry (by the ACS Green Chemistry Institute)

- **Prevention of waste**
  It is better to prevent waste than to treat or clean up waste after it has been created.

- **Less Hazardous Chemical Syntheses**
  Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.

- **Safer Solvents and Auxiliaries**
  The use of auxiliary substances (e.g., solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.

- **Design for Energy Efficiency**
  Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.

- **Inherently Safer Chemistry for Accident Prevention**
  Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.
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CABB’s Verbund and recycling system

Building blocks

non-exclusive

Intermediate, advanced intermediates and actives

exclusive

HCl

SO₂

Cl₂  HCl  H₂  CISO₃H  SOCl₂  SO₂Cl₂  CH₃OSO₃CH₃  SO₂  SO₃  H₂SO₄·SO₃

HCl

NaOH

H₂SO₄

Cl₂

SO₃

NaCl

S
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Metrics

Process Mass Intensity (PMI)

\[
PMI = \frac{\text{total mass of incoming materials in a process (incl. solvents and water) [kg]}}{\text{total amount of product [kg]}}
\]

Environmental factor

\[
E\text{-factor} = \frac{\text{total mass of waste [kg]}}{\text{total amount of product [kg]}}
\]

Source: C&EN, May 28, 2012, p.20
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Case study: Mesylation reaction: batch to continuous

- Reaction of a secondary alcohol with methanesulfonyl chloride in the presence of a tertiary amine in toluene (which is completely recycled)
- Mesylation reaction was originally designed as a batch process
- Reaction was changed into a continuous process
- Same equipment was used
- Further work-up was not modified
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Case study: Mesylation reaction: batch to continuous

Original batch reaction

- Stirring 8 - 9 hrs exothermic
- Continuous work-up

CABB continuous reaction

- Continuous feed
- Hold-up time 5 hrs
- Continuous removal
- Continuous work-up
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Case study: Mesylation reaction: batch to continuous

![Chemical reaction diagram](image)

<table>
<thead>
<tr>
<th></th>
<th>batch</th>
<th>continuous</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electricity</td>
<td>116%</td>
<td>100%</td>
</tr>
<tr>
<td>Steam</td>
<td>106%</td>
<td>100%</td>
</tr>
<tr>
<td>Cooling water</td>
<td>145%</td>
<td>100%</td>
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<tr>
<td>PMI</td>
<td>10.8</td>
<td>7.4</td>
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<tr>
<td>E-factor</td>
<td>8.1</td>
<td>5.4</td>
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</table>

Results:

- Less energy through constant reactor temperature
- Less waste and cooling water
- 20% increase of output per day
- Reduction of amount of toluene
- Batch process: E-factor is 50% higher; PMI is 46% higher than continuous
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Case study: Chlorination reaction

- Acid chloride formation
- Reaction of a carboxylic acid with thionyl chloride
- Thionyl chloride is an inexpensive, transportable, easy-to-handle and commonly used chlorination reagent
- HCl and SO₂ are generated as off-gases
- First part: batch vs continuous process
- Second part: scrubber vs CABB's Verbund and recycling system
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Case study: Chlorination reaction: batch vs continuous process

- Comparison of acid chloride formation with thionyl chloride in batch vs continuous process
- Removal of off-gases not considered
- Based on identical production volumes and same stoichiometry
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Case study: Chlorination reaction – batch vs continuous

\[
\begin{align*}
R\text{COOH} & \xrightarrow{\text{SOCl}_2} R\text{COCI} \\
& \quad \left( + \text{HCl} + \text{SO}_2 \right)
\end{align*}
\]

<table>
<thead>
<tr>
<th></th>
<th>batch</th>
<th>continuous</th>
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</thead>
<tbody>
<tr>
<td>Electricity</td>
<td>140 %</td>
<td>100%</td>
</tr>
<tr>
<td>Steam</td>
<td>128 %</td>
<td>100%</td>
</tr>
<tr>
<td>Cooling water</td>
<td>166 %</td>
<td>100%</td>
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</table>

Results:
- Less energy required in continuous reaction
- Less cooling water required in continuous reaction
- Higher throughput in continuous reaction
- Lower cost of production
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Case study: Chlorination reaction: scrubber vs recycling system

- SO$_2$ and HCl are generated as off-gases
- For better comparison both reactions are carried out as batch process
- Removal of off-gases:
  - conventional scrubber (neutralisation with caustic soda → waste water)
  - CABB’s recycling system (SO$_2$ is recycled into SO$_3$, HCl is converted into hydrochloric acid)
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Case study: Chlorination – scrubber vs Verbund

\[
\begin{align*}
\text{R} & \quad \text{SOCl}_2 & \quad \text{R} & \quad \text{Cl} & \quad + & \quad \text{HCl} & \quad + & \quad \text{SO}_2 \\
\text{OH} & \quad & \quad & \quad & \quad & \quad & \quad & \\
\end{align*}
\]

<table>
<thead>
<tr>
<th></th>
<th>scrubber</th>
<th>Verbund</th>
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</thead>
<tbody>
<tr>
<td>Electricity</td>
<td>142 %</td>
<td>100%</td>
</tr>
<tr>
<td>Steam</td>
<td>111 %</td>
<td>100%</td>
</tr>
<tr>
<td>Caustic soda</td>
<td>3.7 kg per kg product</td>
<td>0 kg</td>
</tr>
<tr>
<td>Waste water</td>
<td>4.7 kg per kg product</td>
<td>0 kg</td>
</tr>
<tr>
<td>PMI</td>
<td>6.3</td>
<td>2.1</td>
</tr>
<tr>
<td>E-factor</td>
<td>4.7</td>
<td>0.04</td>
</tr>
</tbody>
</table>

**Scrubber:**
- Large volumes of caustic soda required for scrubber process
- Scrubber generates large amounts of waste water containing salts

**Verbund and recycling system:**
- Requires less energy
- Reagent is completely used or recycled
- HCl is converted into hydrochloric acid; SO₂ is completely recycled into SO₃
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Continuous chlorination: quality and side-products

Acid sensitive substrates need scavenger in batch processes
- Less good PMI and E-factor

Continuous processes can be carried out without scavengers:
- Better sustainability
- Better quality of the product
- Constant reaction conditions lead to higher quality
- Less energy requirement
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Continuous standard unit operations: highest efficiency

- Series of continuous standard unit operations in dedicated and multi-purpose equipment
- Set of independent standard unit operations to combine a complete continuous flow process
- Availability of equipment to assemble most efficient production process
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Case study: continuous Wolff-Kishner reaction: process safety

- Wolff-Kishner reaction: reduction of aldehydes and ketones to corresponding aliphatic compound

- Advantages:
  - Selective reduction of the carboxylic function
  - One step from ketone/aldehyde to alkane
  - No metal catalyst

- Challenges:
  - Handling of hydazine
  - Formation of nitrogen
  - Substrate has to be stable under high temperature and basic conditions
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Case study: continuous Wolff-Kishner reaction: process safety

\[
\begin{array}{ccc}
\text{batch} & \text{continuous} \\
\text{PMI} & - & 2.51 \\
\text{E-factor} & - & 1.38 \\
\end{array}
\]

Results:

- Wolff-Kishner can not be realised in batch reaction in commercial scale
- Batch reaction releases nitrogen in large amount „at once“, exceeding a certain temperature
- Intermediate, which releases nitrogen, is present in low concentration only in continuous process
- Continuous reaction releases nitrogen in small amounts per time unit which can be easily removed
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Summary

- CABB has a longstanding expertise and know-how in the design and application of safe, **continuous processes** in large commercial scale, in dedicated and multi-purpose equipment.
- CABB performs chlorination, sulfonation, chlorosulfonation and methylation processes in a highly efficient and **sustainable** way due to its **Verbund and recycling system**.
- CABB can carry out **hazardous chemistry** in a safe way due to closed systems and highly sophisticated infrastructure.
- **CABB combines the advantages of its Verbund and recycling system with multipurpose fine chemical assets at one site**.
Outsource your chemistry to CABB!

Questions, suggestions and comments to:

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