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

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Continuous processes - Sustainable manufacturing

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- Chlorination reaction: scrubber vs. process gas recycling
- Continuous chlorination: quality and side products
- Continuous standard unit operations
- Continuous Wolff-Kishner reaction: process safety

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[1]

[1] Org.Process Res. Dev, DOI: 10.1021/op100327d

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

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- 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

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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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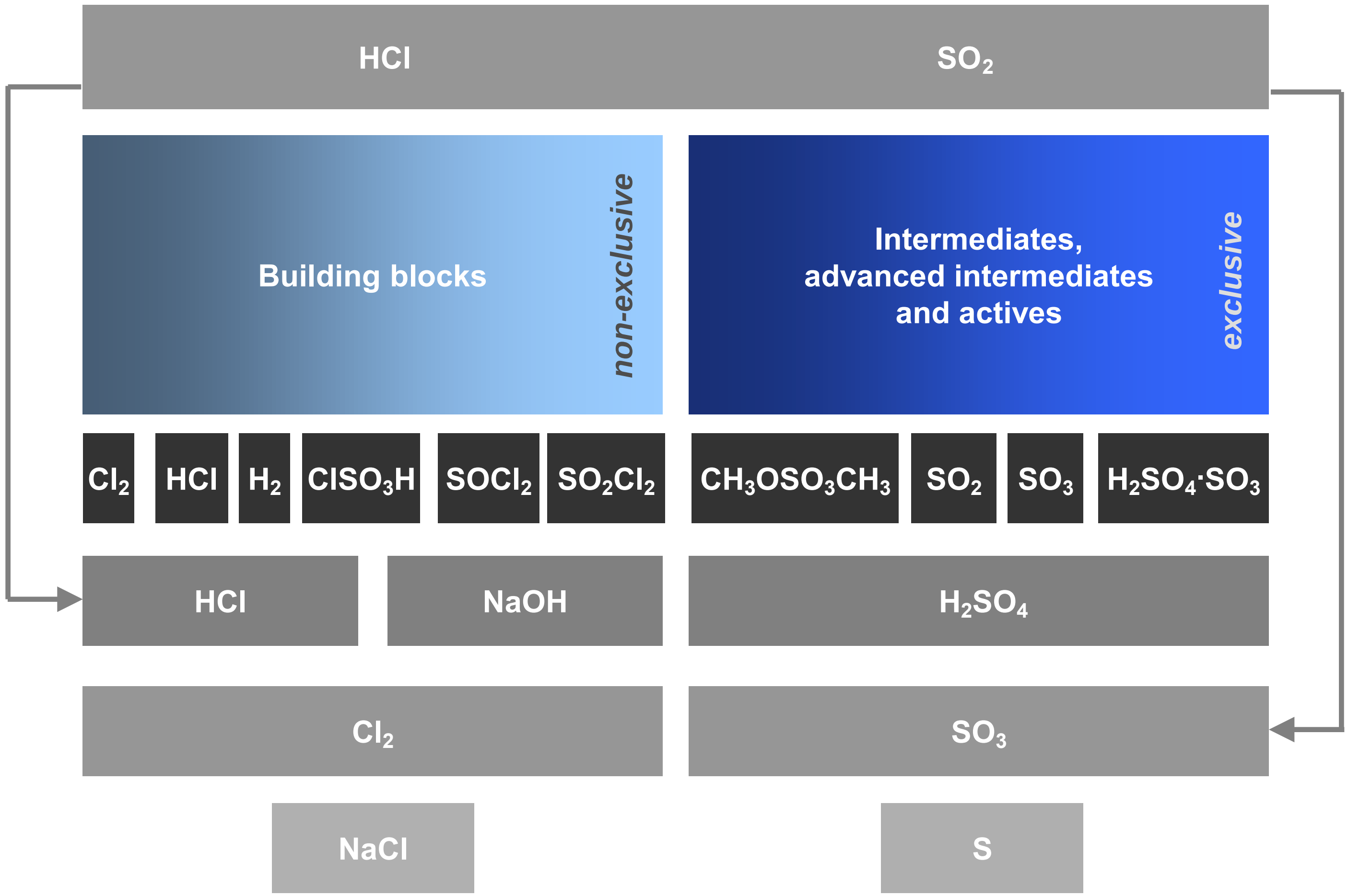
CABB's Verbund and recycling system



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Metrics

Process Mass Intensity (PMI)

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

Environmental factor

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

PROCESS PERFORMANCE

Of 21 pharma and fine chemicals firms surveyed, most use process mass intensity as a metric

METRIC USED	FIRMS USING, %
Process mass intensity	67%
E-factor	48
Atom efficiency	14
Carbon footprint	10
Water usage	10

Source: C&EN, May 28, 2012, p.20

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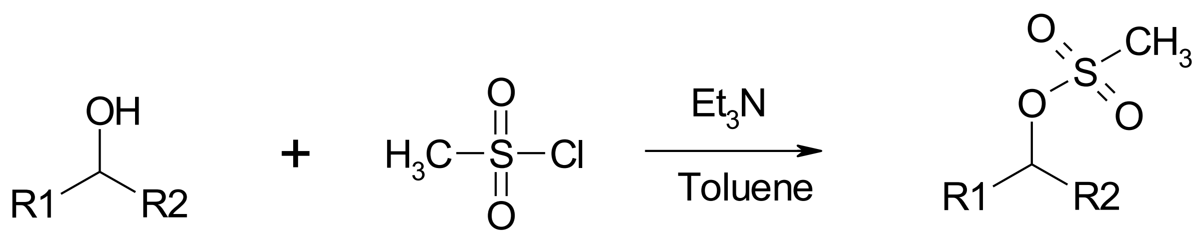
Case study: Mesylation reaction: batch to continuous



- 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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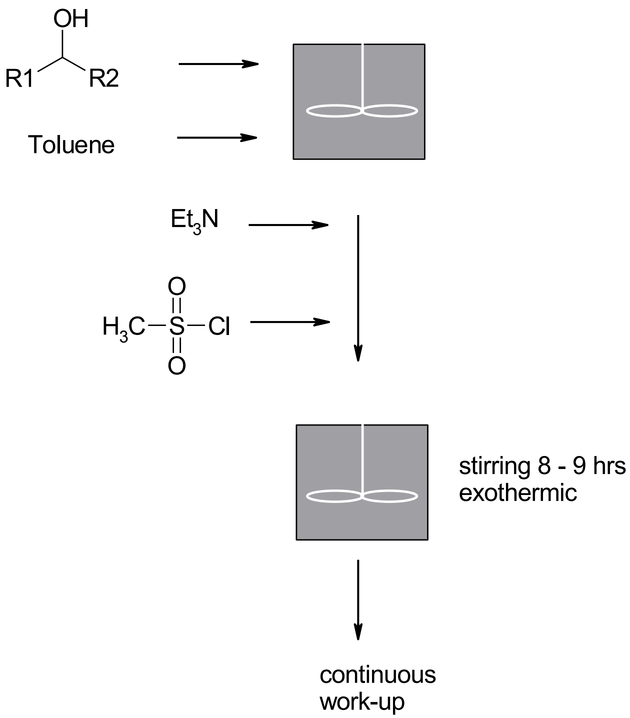
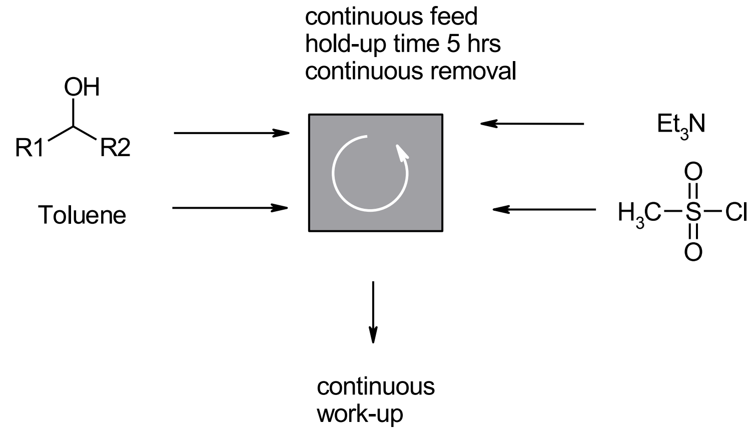
Case study: Mesylation reaction: batch to continuous

Original batch reaction



CABB continuous reaction



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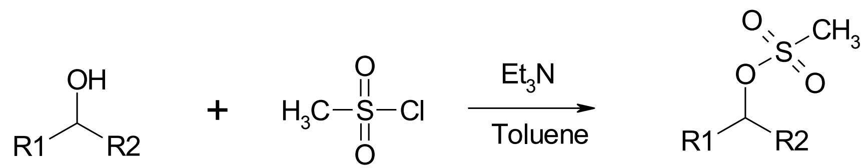
Case study: Mesylation reaction: batch to continuous



	batch	continuous
Electricity	**116%**	**100%**
Steam	**106%**	**100%**
Cooling water	**145%**	**100%**
PMI	**10.8**	**7.4**
E-factor	**8.1**	**5.4**

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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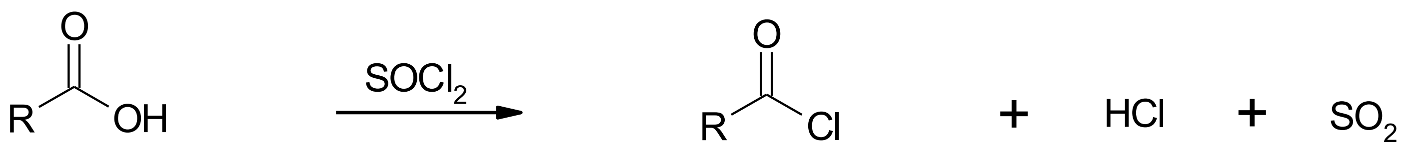
Case study: Chlorination reaction



- 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 SO_2 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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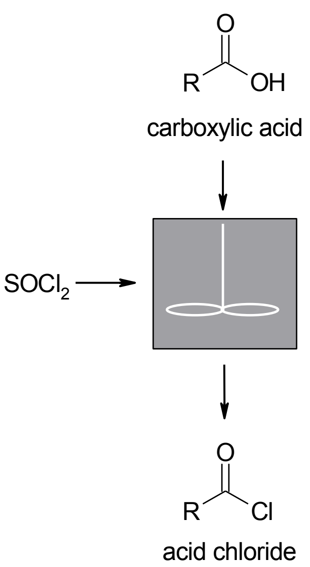
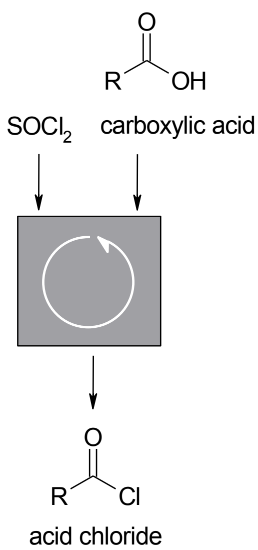
Case study: Chlorination reaction: batch vs continuous process

Conventional batch chlorination



Chlorination in 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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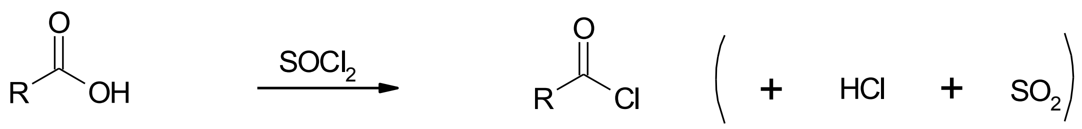
Case study: Chlorination reaction – batch vs continuous



	batch	continuous
Electricity	**140 %**	**100%**
Steam	**128 %**	**100%**
Cooling water	**166 %**	**100%**

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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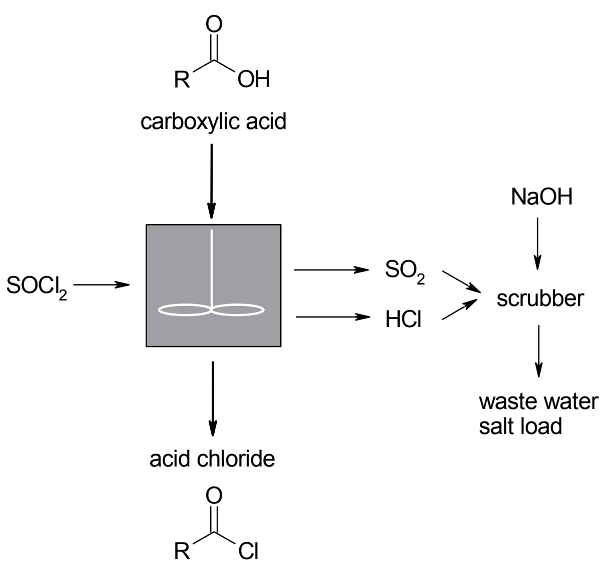
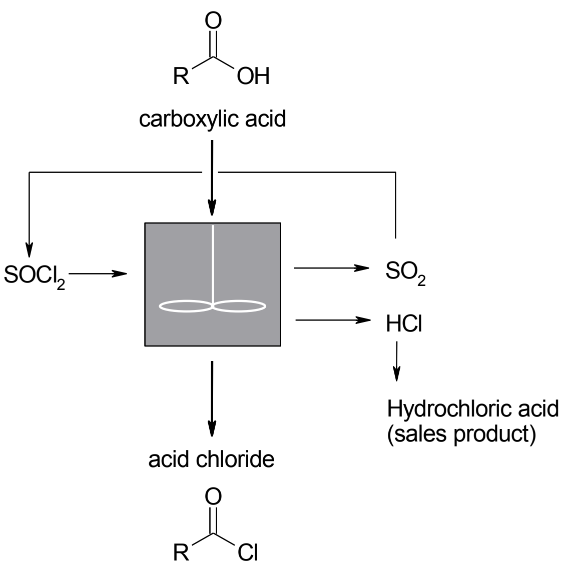
Case study: Chlorination reaction: scrubber vs recycling system

Conventional chlorination with scrubber



Chlorination at CABB's Verbund 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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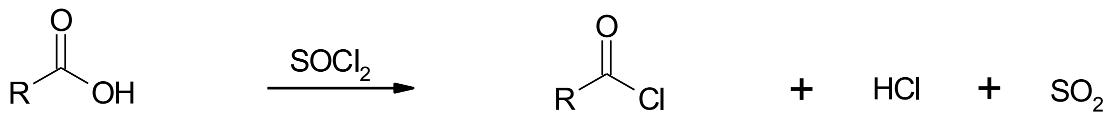
Case study: Chlorination – scrubber vs Verbund



	scrubber	Verbund
Electricity	**142 %**	**100%**
Steam	**111 %**	**100%**
Caustic soda	**3.7 kg per kg product**	**0 kg**
Waste water	**4.7 kg per kg product**	**0 kg**
PMI	**6.3**	**2.1**
E-factor	**4.7**	**0.04**

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; SO_2 is completely recycled into SO_3

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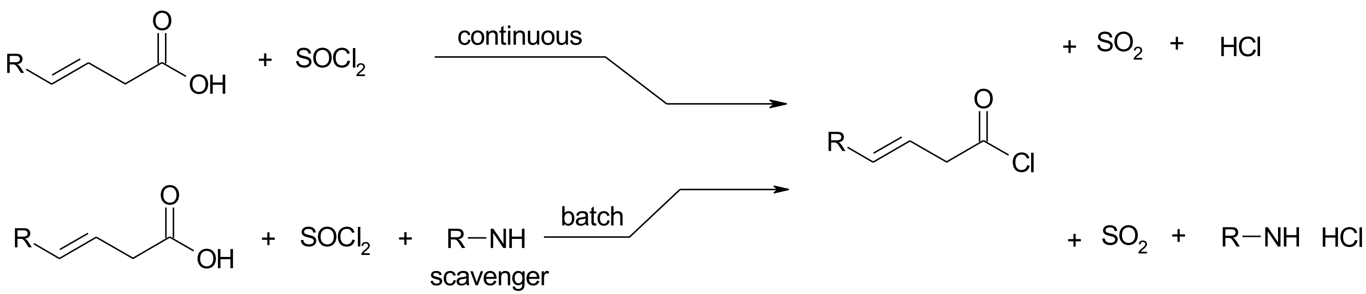
Continuous chlorination: quality and side-products



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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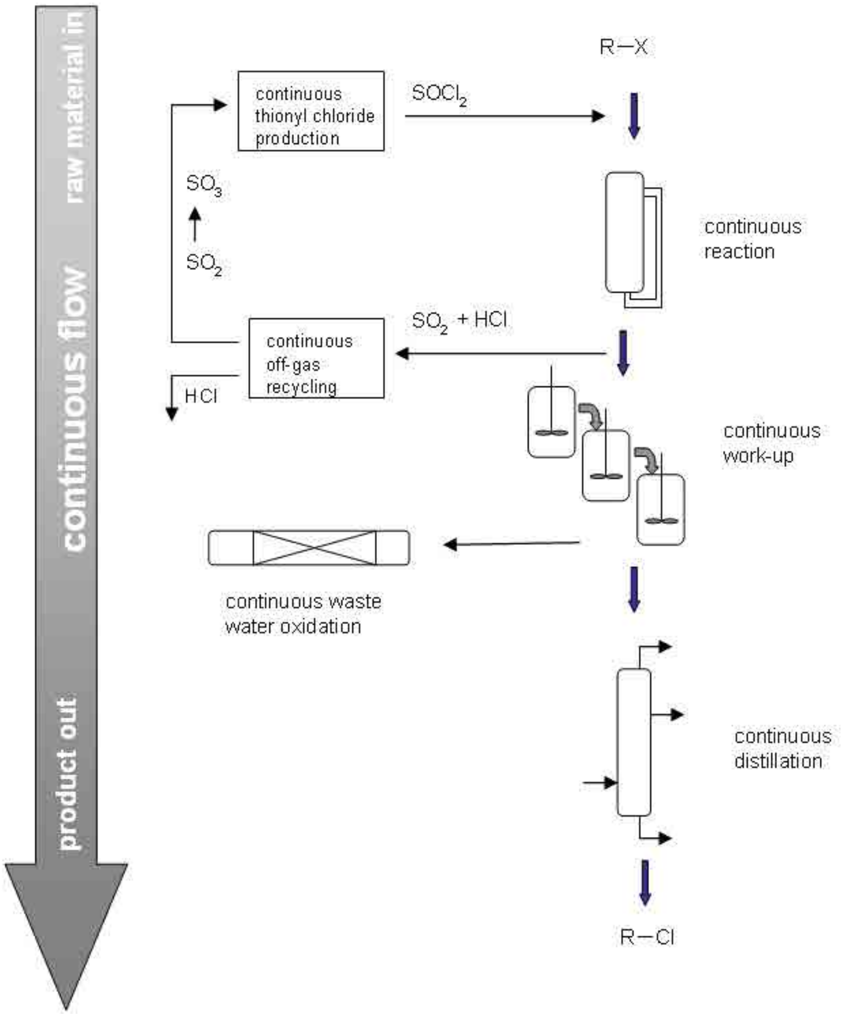
Continuous standard unit operations: highest efficiency



- 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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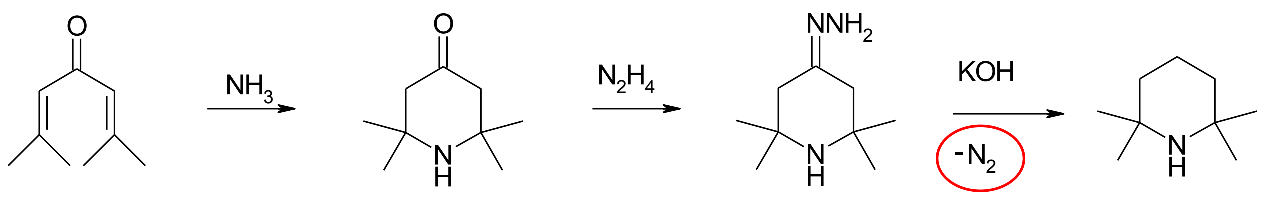
Case study: continuous Wolff-Kishner reaction: process safety



- 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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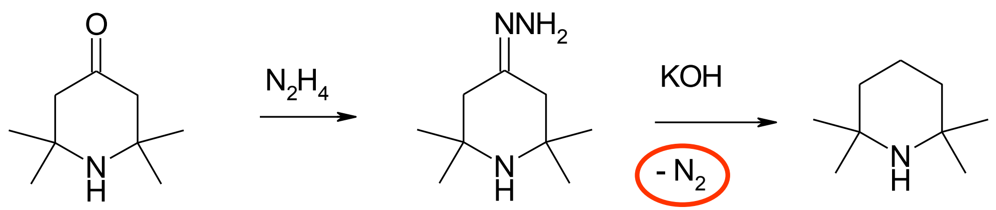
Case study: continuous Wolff-Kishner reaction: process safety



	batch	continuous
PMI	**-**	**2.51**
E-factor	**-**	**1.38**

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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