Bewertung der ökologischen Potenziale der Mikroverfahrenstechnik

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Abstract

Mit Hilfe der Methodik der Ökobilanzierung wurde der Frage nachgegangen, inwieweit durch die Überführung chemischer Synthesen von der makro-skaligen diskontinuierlichen in die kontinuierliche Verfahrensweise im Mikrostrukturreaktor ökologische Vorteile erreicht werden können. Als Beispielreaktion diente die zweistufige Herstellung von m-Anisaldehyd aus m-Bromanisol, die zum einen diskontinuierlich im Doppelmantelreaktor und zum anderen kontinuierlich im Cytos® Lab System der CPC Systems GmbH, durchgeführt wurde. Diese Synthese kann aufgrund ihrer starken Exothermie im herkömmlich eingesetzten Batch-Verfahren nur unter erheblichem Sicherheitsaufwand und mit einem hohen Bedarf an Kühlenergie durchgeführt werden.

Die Ergebnisse der Wirkungsabschätzung hinsichtlich der aus beiden Alternativen resultierenden Umweltbelastungspotenziale zeigen – exemplarisch aufgezeigt an der Synthese von m-Anisaldehyd - einen deutlichen ökologischen Vorteil der kontinuierlichen Synthese im Mikrostrukturreaktor. Dies ist insbesondere auf Energieeinsparungen, die Verringerung des Lösungsmittelbedarfes und auch auf eine Erhöhung der Ausbeute zurückzuführen, die zu einer Verminderung des Chemikalieneinsatzes um insgesamt 166kg bei der Synthese von 10kg m-Anisaldehyd führt. Die Bereitstellung der Peripherie spielt demgegenüber eine untergeordnete Rolle. Bei häufigem Austausch des Mikrostrukturreaktors kommen jedoch Toxizitätspotenziale zum tragen, die aus der Edelstahlproduktion resultieren.

Assessment of the Ecological Potential of Microreaction Technology

1. LCA-Workshop, Bad Urach, 15.06.05

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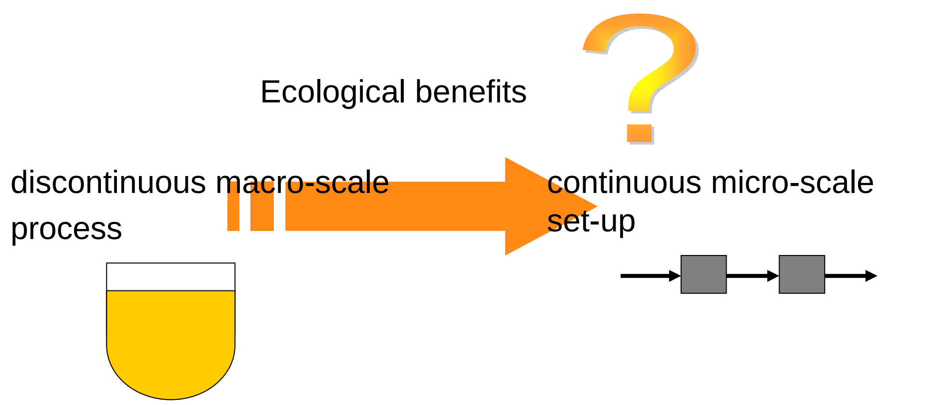
Introduction



Pros:

- Increased surface-to-volume ratios lead to lower cooling- and heating power requirements
- Excellent control of heat transfer may result in higher yields and selectivity of chemical conversions

Cons:

- The manufacture of microreactors can be more material- and energy consuming (especially for the production of micro-structured devices from stainless steel)
- microreactors might have shorter lifetimes e.g. due to clogging phenomena in the microchannels

↳ **Life Cycle Assessment (LCA)**

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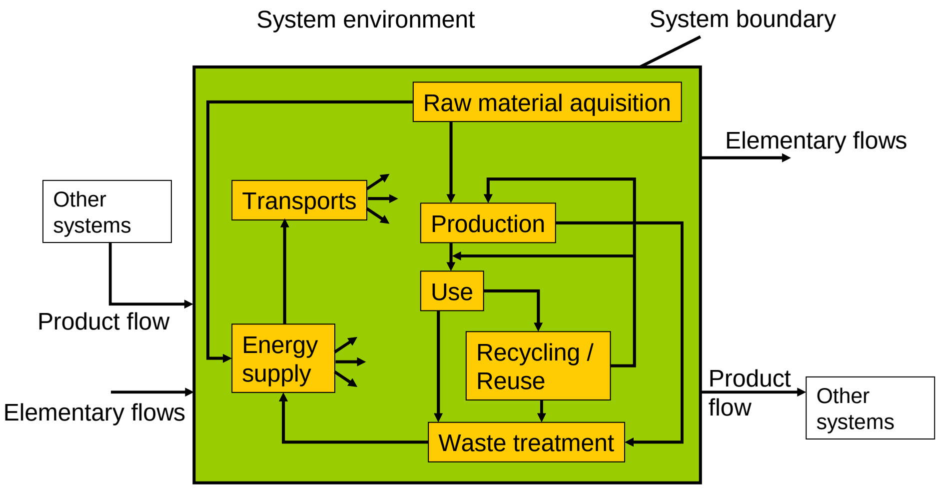
Life Cycle Assessment (LCA)

- Methodological framework for estimating and assessing the environmental impact attributable to the life cycle of a product
- standardized by EN ISO 14040 to 14043
- It is divided into four parts:
  - Goal and scope definition
  - Life cycle inventory (LCI)
  - Life cycle impact assessment (LCIA)
  - Interpretation

Life cycle inventory (LCI)



DIN EN ISO 14041 : 1998

Life cycle impact assessment (LCIA)

Material and energy flows → Environmental impact potentials

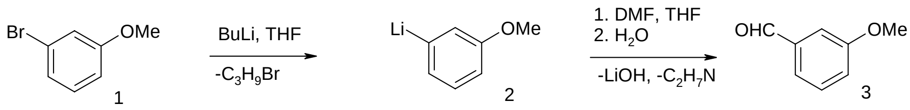
Impact categories considered:

- Global warming (GWP)
- (Stratospheric) ozone depletion (ODP)
- (Tropospheric) photochemical ozone creation (POCP)
- Acidification (AP)
- Eutrophication (NP)
- Human toxicity (HTP)
- Ecotoxicity (ETP)
- Land use

$$IP = \sum_{i=1}^{n} m_i \cdot IF_i$$

m = mass
IF = impact factor

The model reaction and its realization



Stage I

m-bromoanisole (1) and *n*-butyllithium are converted *via* bromo/lithium exchange to yield *m*-lithium anisole (2) and *n*-bromobutane.

Solvent: tetrahydrofurane

Stage II

the reaction mixture is treated with the electrophilic dimethylformamide to produce *m*-anisaldehyde (3), after which the reaction is quenched using 3M hydrochloric acid

T. Schwalbe, V. Autze, M. Hohmann, W. Stirner; Org. Proc. Res. & Dev. **2004**, 8, 440-454

The discontinuous experiment

- Reactor: 10 L double-walled reactor (QVF)
- Temperature: < - 58°F (323.15 K)
- Yield: 60 % of the theory (0.4 kg within 11.5 h)
- Purity: 96 % (GC)

The continuous mode

- Reactor: two Cytos®-Lab-System modules (CPC Systems) connected in series
- Temperature: 32°F (373.15 K)
- Yield: 88 % of the theory (1.4 kg) after a run-time of 24 h
- Purity: 96 % (GC)

- Work-up (both): by phase separation an 3 distillation steps

Demand of chemicals

Demand [kg] for synthesis of 10 kg *m*-anisaldehyde	Continous micro-scale process	Batch process
n-butyllithium (1.6 M in n-hexane)	38	58
m-bromanisole	16	24
3M hydrochloric acid	62	93
dimethylformamide	9	12
acetone	-	52
tetrahydrofurane	50	102
methanol	0.5	-

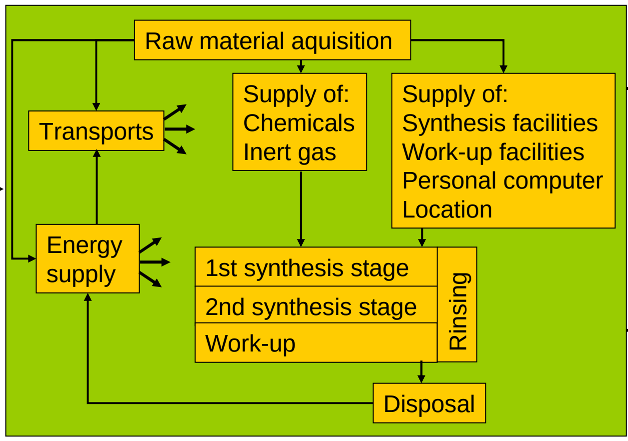
Scenarios concerning lifetime of microreactors

Scenario	Reactor	Presumed lifetime
Conti_Sc_wc	Cytos®	1 week
Conti_Sc1		3 month
Conti_Sc2		3 years
Conti_Sc3		30 years
Batch	10 L double walled	30 years

System boundary

Elementary flows:

raw materials from their deposits, renewable resources, area use



Elementary flows:

emissions into the compartments air, water, soil

m-Anis-aldehyde

Selected results of the LCIA

Global warming potential (GWP)

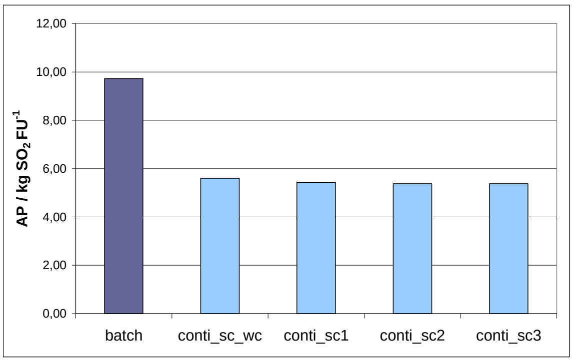
functional unit (FU) = 10 kg of *m*-anisaldehyde

Reference: CO_2

Greenhouse gases considered:
CO_2, CH_4, CCl_3F, CCl_2F_2, CF_4

➡ Reduction of the GWP by 52 to 57 %

Acidification potential (AP)



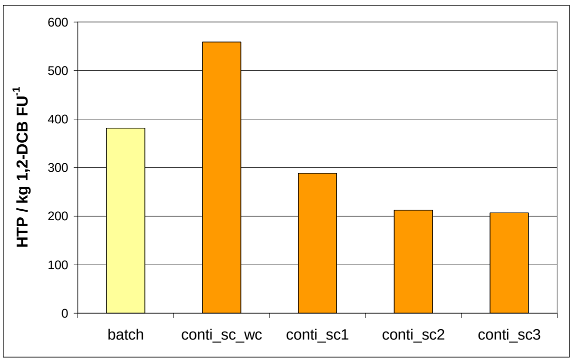
Functional unit (FU) = 10 kg of *m*-anisaldehyde

Reference: SO_2

Substances considered:
SO_2, NO_x, NH_3, HCl, HF

➡ Reduction of the AP by 42 to 45 %

Human toxicity potential (HTP)



Functional unit (FU) = 10 kg of *m*-anisaldehyde

Reference:
1,2-dichlorobenzene (DCB) according to Huijbregts et al.*

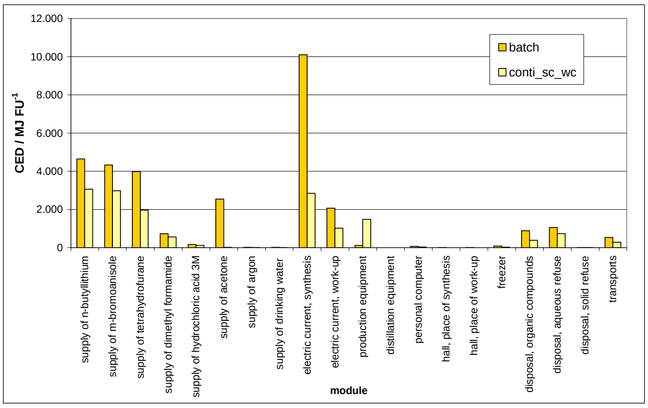
Substances considered:
Heavy metals:
Sb, As, Ba, Be, Pb, Cd, Cr III, Cr VI, Co, Cu, Ni, Hg, Se, Tl, V
Inorganic compounds:
NH_3, HCl, SO_2, NO_x
Organic compounds:
Benzo(a)pyrene, benzene, hexachlorobenzene and PAH

* M.A.J. Huijbregts, U. Thissen, J.B. Guinée, T. Jager, D. Kalf, D. van de Meent, A.M.J. Ragas, A. Wegener Sleeswijk, L. Reijnders, Chemosphere **2000**, 41, 541

➡ Variation of the HTP by +47 to -46 %

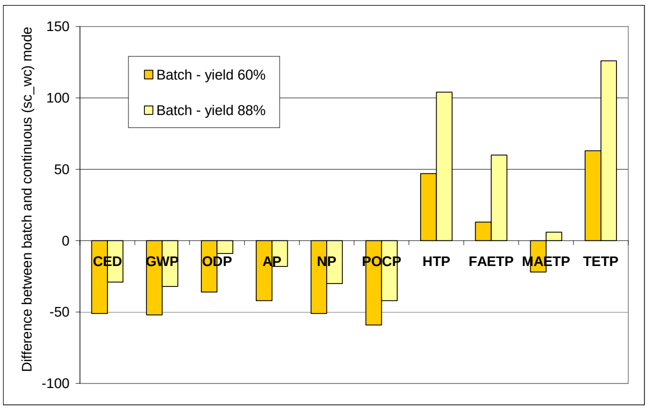
Interpretation

Sensitivity analysis – breakdown of the CED



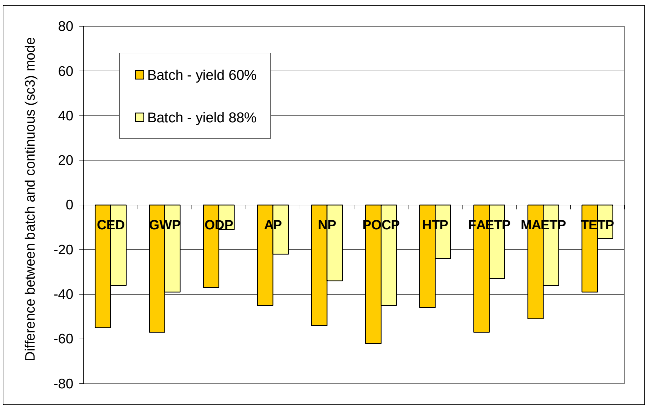
Breakdown of the cumulative energy demand of the scenarios „batch“ and „worst case continuous“ mode in single modules

Sensitivity analysis - influence of the yield



Alterations of each impact category for batch-mode yields of 60 and 88 %, resulting from the transfer to the continuous Cytos® Lab System for the „worst case“-scenario

Sensitivity analysis - influence of the yield



Alterations of each impact category for batch-mode yields of 60 and 88 %, resulting from the transfer to the continuous Cytos® Lab System for the best-case-scenario “cont_Sc3”

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Conclusions

- significant ecological advantages associated with the continuous synthesis in the microreactor for this specific case, because of:
  - savings in energy consumption
  - reduction of educts and solvents
  - increase of reaction yield
- the fabrication of reactors, thermostats, distillation units *etc*. only play a minor role
- frequent exchange of microreactors leads to increased toxicity potentials, resulting from the stainless steel production
  - special attention should be paid to a long life cycle of the microstructured devices from stainless steel

Outlook

Mini-plant scale → industrial scale

Acknowlegdement

- Deutsche Bundesstiftung Umwelt
- CPC Systems GmbH
- Bayer AG