A Deliberate Green Process Design in Microstructured Reactors by Accompanying (Simplified) Life Cycle Assessment

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Process intensification via continuously running syntheses in microstructured reactors offers new possibilities to realize environmentally benign chemical processes. To evaluate the environmental impacts induced by the reactions under investigation, a research accompanying life cycle assessment (LCA) has been applied in several projects dealing with process intensification in microreactors. The same adapted method was applied during the development of a phase transfer catalytic process in microstructured reactors giving phenyl benzoate. It could be shown that the overall life cycle impact of this reaction highly depends on the yield of phenyl benzoate, but can be significantly improved by the implementation of ionic liquids as phase transfer catalysts compared to the same reaction without implementing any catalyst.

1. Introduction

In the last years huge efforts have been made regarding the development of sustainable processes and products including, e. g., the substitution of petrochemical products by renewable materials, implementing catalysts, novel reaction media and/or alternative energy sources as well as process intensification (PI). Microstructured reactors have been identified as suitable tools for realizing PI due to their high surface-to-volume ratio which enables very efficient heat and mass transfers. Further, the inherent small inner volumes allow for a safer handling of hazardous or toxic substances and may also lead to a reduction of solvents required. Thus, reaction conditions as well as residence times can be adapted very precisely to the reaction under investigation leading to high yields and selectivities (Mason et al., 2007). Due to the compact and modular design including pumps and controlling instruments, microreactor plants are used in research and development (R&D) taking advantage of their high flexibility, but are also increasingly implemented in industrial production processes (Schmalz et al., 2005).
In order to support these "green" approaches, several metrics and methods have been developed to investigate and quantify the environmental burdens caused by a product or

process, e. g., atom economy (Trost, 1995), E-Factor (Sheldon, 1994), EHS method (Koller et al., 2000). However, the most comprehensive method used for environmental evaluation is the life cycle assessment (LCA) standardized in the ISO norms 14040 and 14044 (ISO 2006a, b). By this method, the whole life cycle of a product or process is investigated from the exploitation of raw materials and supply of energy to the disposal of process wastes and recycling of recyclable materials, solvents or catalysts.

Usually, LCAs are performed for already established processes or at least in the pilot-plant stage because R&D stages are often regarded as contributing only marginally to the overall environmental burdens (Rebitzer et al., 2004). But, environmental impacts often become predefined by the decisions made during R&D and process design (Kheawom and Hirao, 2002). Further, subsequent reductions of environmental burdens by end-of-pipe solutions are often associated with high expenses (Biwer and Heinzle, 2001). Main hurdles for performing LCAs in those early stages are the high data requirements according to the ISO norms since data gaps and uncertainties are inherent to R&D. However, as environmental assessment methods are regarded as being efficiently applied starting already in R&D (Zhang et al., 2008), multiple methods have been developed explicitly for application in R&D, e. g., euroMat (Fleischer and Schmidt, 1997), ECO method (Kralisch et al., 2007) as well as a 4-ary algorithm by Sugiyama et al. (2008). These methods represent various possibilities of simplified life cycle assessment (SLCA) dealing with the scarce information available initially in research activities.

Currently, several research activities dealing with PI in microstructured reactors are funded by the German Federal Environmental Foundation (Deutsche Bundesstiftung Umwelt, DBU). In these projects, PI is realized via the application of harsh reaction conditions, i. e., high temperatures, high pressures and/or high concentrations. Further concepts for achieving PI are the implementation of alternative solvents like ionic liquids (IL) or supercritical media as well as the application of non-conventional energy forms, e.g., ultrasound or microwave irradiation. Some of these projects are accompanied by (simplified) life cycle assessment supporting the development of environmentally benign chemical processes. (Huebschmann et al., 2009; Stark et al., 2009) The methods applied as well as some results are presented next.

2. Methods

In all research projects investigated, the experimental activities were started with the investigation of the batch synthesis in lab scale in order to establish an internal benchmark. Afterwards, the reaction set-up was transferred to a microreactor plant and optimized consecutively. Both, the batch as well as the continuously running reactions are evaluated by life cycle assessment and compared with each other to derive an optimization potential.

The environmental assessments are performed in accordance with the ISO norms 14040 and 14044. Umberto[®] (Umberto 2008) in conjunction with the Ecoinvent[©] database (Ecoinvent 2009) is used as software to model the mass and energy flows. Further, the mid-point indicators proposed by Guinée (2001) as well as the cumulative energy demand (CED) (The Association of German Engineers, 1997) were applied to evaluate the environmental burdens.

However, there are several data gaps occurring in R&D, e.g., the energy consumption of the process is often not measured. Further, yields are mostly analyzed directly from the reaction mixture after the reaction was quenched without application of any work-up procedures. Usually, only major solvent fractions are recycled in laboratory scale by distillation whereas small amounts of catalysts and/or solvents are disposed.

Thus, we are simplifying the LCA in R&D first, following the desimplification approach suggested by SETAC working group (SETAC, 1997). By this, we start with the initially scarce experimental data filling the occurring data gaps with the calculation of mass and energy balances or by using generic data. More detailed information is implemented gradually in the SLCA as more knowledge is obtained during subsequent investigations. In order to support the decision making during the process development, scenario analyses are performed, too, since these are powerful tools to explore the influences of certain reaction conditions on the overall life cycle impact of the system studied and to estimate the environmental burdens of possible future developments (Finnveden et al., 2009). In addition, we appraise the robustness of the LCA with respect to potential fluctuations of experimental results by means of sensitivity analysis. For reasons of time efficiency we merely apply the impact categories "Human Toxicity Potential" (Guinée, 2001) and "Global Warming Potential" (Guinée, 2001) as well as the CED as key indicators in our SLCA approach during R&D. Finally, when the process is known in detail, a holistic LCA considering all indicators suggested by Guinée is performed.

3. Results

The case study discussed here deals with continuously running phase transfer catalyses of benzoyl chloride and phenol giving phenyl benzoate (Figure 1). The microreaction plant used in this case study was specifically designed by mikroglas chemtech GmbH, Mainz, Germany, addressing the requirements of automated phase transfer catalyses. The experimental work was carried out at the working group of H. Loewe, Johannes Gutenberg University, Mainz, Germany. The aim of this cooperative project was the transfer of phenol from the aqueous to the organic phase utilizing ionic liquids as phase transfer catalysts (PTC).

For this purpose, the performances of the continuously running syntheses in an interdigital mixer were investigated using two ionic liquids, 1-butylsulfonate-3-methyl-imidazolium ([MIM][BuSO$_3$]) and 1-octadecyl-3-methylimidazolium bromide ([C$_{18}$MIM]Br), as PTC (IR-[C18MIM]Cl and IR-[MIM][BuSO3]) and compared with a scenario without the implementation of a PTC (IR-wC). These results were further opposed to the synthesis carried out as batch reactions with and without implementation of 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) as PTC (B-[BMIM]Cl and BwC). For all scenarios, both, the reaction energy as well as the energy for solvent recycling, were estimated based on thermodynamic data. The reaction conditions applied are summarized in Table 1. The functional unit (FU) chosen for SLCA investigations was defined as 1 kg of phenyl benzoate.

The Global Warming Potential (GWP), Figure 2, in case of the batch reactor can be reduced by 10 % by the implementation of [BMIM]Cl (scenario B-[BMIM]Cl compared to scenario BwC). In case of the continuously running syntheses, the GWP

was reduced by 80 % using [C$_{18}$MIM]Br (IR-[C18MIM]Br) and by more than 85 % using [MIM][BuSO$_3$], respectively, compared to the continuous synthesis without the implementation of a PTC (scenario IR-wC). However, the best environmental reaction performance of all scenarios considered was obtained by the continuous synthesis with
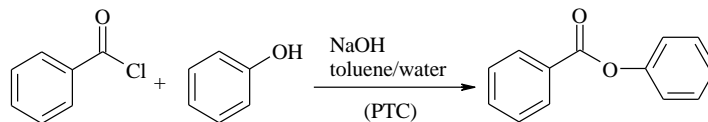

Figure 1: Phase transfer catalysis of benzoyl chloride and phenol giving phenyl benzoate.

Table 1: Reaction conditions for phase transfer catalysis of benzoyl chloride and phenol giving phenyl benzoate in batch syntheses and under utilization of an interdigital mixer.

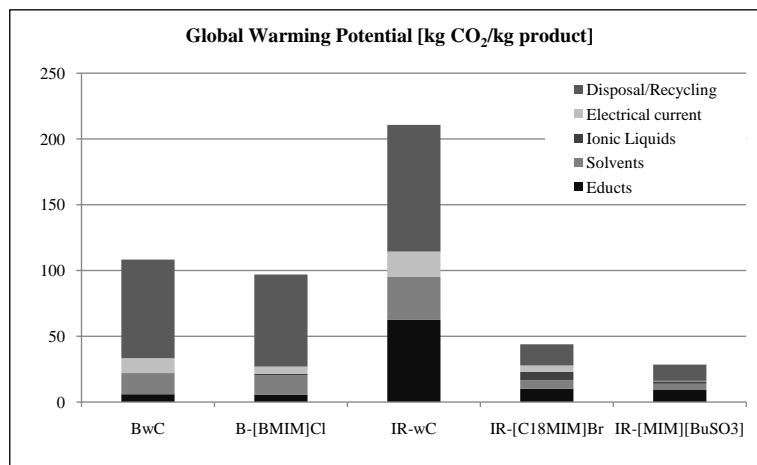| Scenario	Temperature [°C]	Catalyst	Yield [%]
BwC	66	-	66
B-[BMIM]Cl	45.5	[BMIM]Cl	72
IR-wC	57	-	10
IR-[C18MIM]Br	75	[C$_{18}$MIM]Br	62
IR-[MIM][BuSO3]	30	[MIM][BuSO$_3$]	68

Figure 2: GWP of synthesis of phenyl benzoate under various phase transfer conditions.

implementation of [MIM][BuSO$_3$] (IR-[MIM][BuSO3]). A further advantage of [MIM][BuSO$_3$] is the low temperature at which the yield was obtained resulting in a low energy consumption, too.

Apart from the recycling of the solvent toluene, there have not been applied any work-up procedures yet, as the reaction yields were determined directly from the reaction mixture. But, current experiments are focused on the substitution of the aqueous phase by a suitable ionic liquid and the separation of the two phases by the implementation of separation modules into the microreactor plant. At low flow rates, triangular shaped separation chambers separating two liquids by density or Y-shaped modules with one branch hydrophobically modified may be suitable work-up devices for multi-phase reactions (Dietrich et al., 2010). The latter is especially privileged for plug-flow processes. Further experimental investigations will reveal which separation modules are preferably implemented in the model synthesis.

4. Conclusions

A method for accompanying (S)LCA has been described considering the specific characteristics of R&D stages, e. g., data gaps and uncertainties. The method was used to assess the phase transfer catalysis of phenol and benzoyl chloride giving phenyl benzoate and selected results were discussed within this paper. As was shown by this case study, the reaction yield is a crucial parameter for the overall life cycle performance of the reaction under investigation. But, this may not be generalized as in other reaction types other parameters may become significant as can be seen, e. g., in Stark et al. (2009), where the up-stream processes of the reactive media implemented in Kolbe-Schmitt synthesis are dominating the environmental performance of the reaction.

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