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Sustainable Chemistry at the Universities of Applied Sciences

Pauline Sanglard[a], Frank Rogano[a], Olivier Naef[a], Wolfgang Riedl[b], Simon Crelier[c], Fabian Fischer[c], Franziska Morganti[d], and Christian Hinderling*[d]

*Correspondence: Prof. Dr. C. Hinderling[d], Tel.: +41 58 934 55 10, E-mail: christian.hinderling@zhaw.ch
[a]HES-SO Fribourg, University of Applied Sciences Fribourg, Ecole d'ingénieurs et d'architectes, Institut de Chimie, Boulevard de Péroles 80, CP 32, CH-1705 Fribourg
[b]University of Applied Sciences Northwestern Switzerland, School of Life Sciences, Institute for Chemistry and Bioanalysis, CH-4132 Muttenz
[c]Institute of Life Technologies, University of Applied Sciences Western Switzerland, HES-SO Valais, Sion
[d]Zurich University of Applied Sciences, Institute of Chemistry and Biological Chemistry, Campus Grüental, P.O. Box, CH-8820 Wädenswil

Abstract: An overview of activities in the field of sustainable or 'green' chemistry at the Universities of Applied Sciences in Switzerland is presented.

Keywords: Biochemical engineering · Green chemistry · Sustainable chemistry · Universities of Applied Sciences

Introduction

Industrial chemistry has developed over the past approximately 150 years in an environment of readily available resources, in which most processes have been based on open cycles. Growing ecological concerns and accidents involving dangerous chemicals have led to a problematic public perception of the industry.[1] The implementation of the 'responsible care' initiative by the industry as well as tighter regulations, legislation and waste stream purification were important improvements. In addition, the UNESCO Year of Chemistry in 2011 has certainly helped to improve the public perception of chemistry further, and increased the public awareness of the central role that chemistry is playing in enabling industrial development and growth.

However, a rapidly growing world population and adoption of a resource-intensive lifestyle by a rising percentage of the population is exhausting non-renewable resources rapidly and at a growing pace, making further development along this path questionable at best. The need for more sustainable, efficient, cleaner and 'greener' technologies has been recognized, and is ever more rapidly becoming a pressing economical and ecological need. Research and development into these areas is being promoted both on a national and international level (some examples are: The Masterplan Cleantech from the Swiss federal departments EVD and UVEK, the 'cleantech by biotech' initiative of the 'swiss biotech association' and 'scienceindustries Switzerland', the NFP 66 on resource wood and the Horizon 2020 framework program of the European commission, in which 'advanced manufacturing and processing' and 'biotechnology' are designated key enabling technologies).

For the field of industrial chemistry, the 12 principles of green chemistry have been formulated as guiding principles.[2] These can be briefly stated as preventing pollution at the source, employing atom economy, using processes with less hazardous chemicals, designing safer products, minimizing solvent use and using safer solvents, designing energy efficient processes, using renewable feedstock, reducing derivatives or designing reaction sequences to minimize protection/deprotection sequences, using catalysis, designing degradable products, utilizing real-time analysis for pollution prevention, and designing inherently safe chemical processes.

A somewhat loose interpretation of these points would be a) using fewer chemicals, solvents and energy, b) utilizing safe raw materials, processes and solvents, c) using efficient processes, catalyzed processes, and processes without waste and without derivatization, d) monitoring waste generated in real time, and (e) ensuring that chemical and raw materials are renewable.

Three things become immediately evident. Firstly, sustainable chemistry is dealing primarily with manufacturing processes, where expenditures relating to materials and energy are likely to be high. Secondly, at the very heart of sustainable chemistry is design – the design of the overall process and products, rather than the selective optimization of critical points in a process or the development of a slightly better product. Finally, biocatalyzed processes are very well aligned with these principles and therefore hold much promise.

The chemical industry in Switzerland operates in an environment of expensive resources and high standards regarding ecology, where production processes have to be highly optimized in order to be viable. The implementation of sustainable chemical processes will in consequence likely become a must.

For the Universities of Applied Sciences the area of sustainable chemistry is of particular importance: Our graduates have a background in chemistry as well as in chemical engineering, which optimally prepares them to assume responsibilities in process development, production and scale-up, areas that are situated at the very core of sustainable chemistry. By providing this new generation with the tools and concepts needed to create more sustainable processes, we are helping to promote green chemistry in Switzerland and secure the employability of our graduates.

Some of the activities of the universities of applied sciences in the context of sustainable chemistry are portrayed in the following.

Ecole d'Ingénieurs de Fribourg: Energy-efficient Production of Methanol from Carbon Dioxide

With the stepwise exit from nuclear power and the global shrinking of petroleum and gas reserves, the most important challenge for society in this century will be to satisfy the increasing energy demand. Recycling CO_2 by capture and transformation into a valuable combustible material is an attractive alternative to carbon capture and storage (CCS) technology.

The chemistry group at the engineering school in Fribourg is currently developing a promising new technology for the conversion of CO_2 into methanol. Methanol is a renewable energy vector, which can be easily stored and used as fuel for electric cars (with methanol fuel cells) or as raw material in the chemical industry. We consider CO_2 as a raw material and not as waste. Our innovative approach will help to take up environmental and economic challenges linked with energy issues.

Fig. 1. Hydrogenation reactor.

The well-known capacity of ionic liquids (IL – nonvolatile, easy to handle, sustainable solvents) to absorb CO_2 is being exploited at Fribourg. The complex IL-CO_2 will then be used in a catalytic hydrogenation step to form methanol (Fig. 1). By extraction, methanol can be collected, and the ionic liquid recycled and used again for absorption of CO_2. As hydrogen produced by solar cells is used, the process has a neutral carbon lifecycle.

The HES-SO partners involved in this project are the Ecole d'ingénieurs et d'architectes de Fribourg (EIA-FR), the Haute Ecole d'Ingénierie et de Gestion du Canton de Vaud (HEIG-VD), the Haute école du paysage, d'ingénierie et d'architecture de Genève (hepia) and the HES-SO//Valais.

FHNW Muttenz

Sustainable chemistry is directly linked to innovative and also robust process technologies. One of the main focuses of the chemical engineering group of the Institute for Chemistry and Bioanalytics at the School of Life Sciences in Muttenz is to investigate these technologies. During the last few years, microreactors proved their performance as cross-linking devices between science and application.

The chemical engineering group in Muttenz has used different microreactors for a number of years. A recently investigated application was the reduction of excess alcohol for transesterification of various native oil sources. In order to use fuel generated from native oils in state-of-the-art direct injection engines, oil needs to be broken down to low-chain molecules (*e.g.* raps-methylester). To achieve this, transesterification is commonly used in biodiesel plants worldwide. A by-product of transesterification is (crude) glycerol, which can also be put to the market.

Transesterification is the chemical (batch) reaction of triglycerides with alcohols in the presence of a catalyst and heat, while stirring for a certain amount of time. Since oil and alcohol do not mix well, excess alcohol of up to 40-times the molar ratio needs to be applied in technical operations. This excess alcohol is one of the reasons for the high production costs of biodiesel, since extraction and recycling of alcohol require additional equipment, which generates additional operational costs.

Micro-reaction technology can be used for intensive mixing, continuous reaction and high apparatus surface to process volume ratio. When using micro-reaction for transesterification in continuous operation, it was shown that excess alcohol could be reduced to at least 1:6 oil-to-alcohol molar ratio due to a considerable improvement in mixing (Fig. 2), achieving the same yield at comparable operation times as in conventional transesterification reaction. Scale-up technologies for higher throughput are presently being investigated.

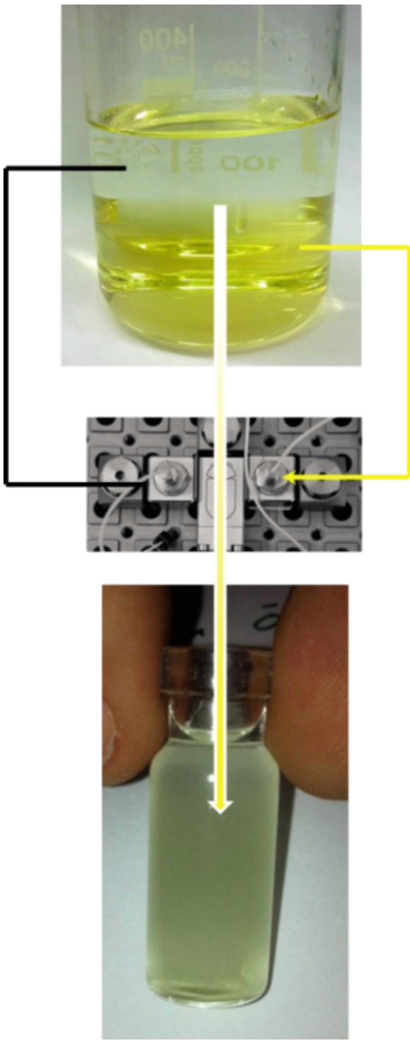

Fig. 2. Poorly miscible native oil and alcohol (top) can be mixed appropriately using microreactor technology.

HES-SO Sion: Algae Oil and Renewable Chemicals

Sequestering carbon dioxide using microalgae is a non-food chain approach to produce renewable chemicals such as biosurfactants, biolubricants, biodiesel and others. CO_2 is available from industrial fermentations, combustion processes and the air. The objective is to produce high oil contents using CO_2 in a concentrated form and sunlight as the sole energy source (Fig. 3).[3] Triacylglycerol extraction from microalgae is also the subject of a detailed investigation as algae cell walls retain accumulated oils very efficiently. For a long time, vegetable lipids have been transformed into renewable commodities such as fatty acids, glycerol, esters and alcohols. A recent development is their biotransformation by lipase-mediated catalysis into performance and specialty chemicals, which was investigated by the biotransformation of fatty acids and methyl-α-D-glucose into biosurfactants using immobilized lipases coated with ionic liquids.[4] In addition, biolubricants from biodiesel or fatty acids and trimethylolpropane were obtained in a solvent-free biphasic lipase catalysis. Adapted process tools are equally required for minimal solvent processing, and a newly designed microwave barrel reactor (MBR) has been constructed and employed for enzymatic biolubricant synthesis.[5] While the subject of investigations was biolubricant, the technology is of wider potential interest in the field of biomass processing and sustainable chemical manufacture.

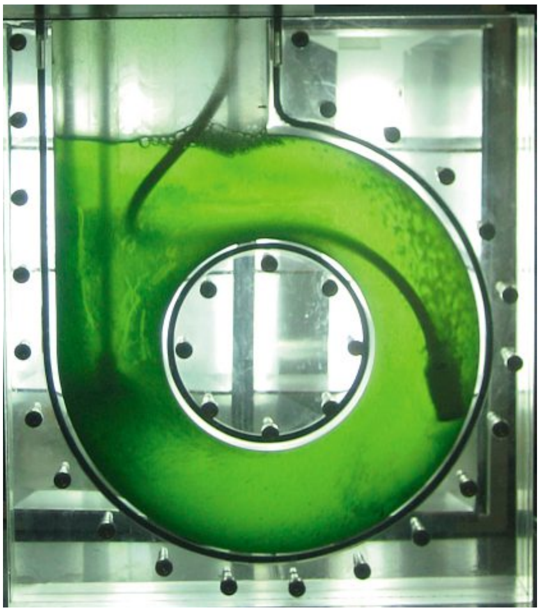

Fig. 3. Torus photobioreactor with micro algae cultivation.

Biosorption: Low-cost Adsorbents for Effluent Decontamination

Biosorption is one contribution to the many efforts presently aiming at the efficient and cost-effective removal of micropollutants by adsorption, using low-cost materials.[6] Several model systems have been investigated at the HES-SO Valais, the studies including aspects such as the formulation and characterization of adsorbent particles, adsorption isotherm and kinetics measurements, as well as elution and regeneration. In a first case, biosorption of Cu^{2+} ions from a model effluent using a combination of dried, powdered algae with chitosan was investigated. The use of chitosan microbeads in a fixed bed was selected since this configuration allows easier manipulation and operation (Fig. 4).[7]

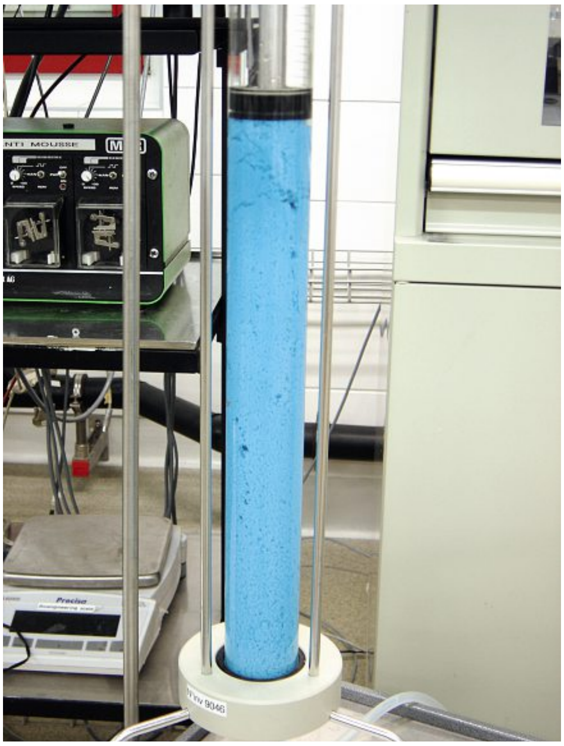

Fig. 4. Cu^{2+} adsorption on a fixed bed of chitosan microbeads.

A similar approach was adopted in order to evaluate the potential of lentil-shaped particles of polyvinylalcohol (PVA) for the entrapment of various biosorbents, the advantage of PVA being an outstanding mechanical resistance which allows its use in stirred tank contactors. Model contaminants such as cadmium ions and carbamazepine were efficiently removed using this approach.[8]

In a last round of investigations, apricot stones were transformed into activated charcoal in a pyrolysis oven. The charcoals obtained were studied with respect to weight loss, specific surface (BET) and particle size. Adsorption isotherm and kinetics were then investigated and modeled using methylene blue and phenol as contaminants, under batch and fixed-bed configurations.[9]

ZHAW Wädenswil

At the Institute of Chemistry and Biological Chemistry (ICBC) at the Zurich University of Applied Sciences, the area of sustainable chemistry figures prominently, both in our teaching and our research activities. Special emphasis is placed on the following three key areas in engineering and process development:

i) Continuous and miniaturized chemical processes

Running chemical reactions in a continuous manner in (miniaturized) flow systems has numerous advantages such as tight reaction control, fast mass and heat transfer, minimization of the amounts of hazardous intermediates, and minimization of solvent use.

ii) Online-analytics and process analytical technologies (PAT)

Having extensive and significant (near) real-time information on running processes allows a reaction to be efficiently controlled. Especially in conjunction with continuous reaction or in bioprocesses, analytical information becomes a controlled process variable instead of a measure of quality at the end of the reaction. Raman, IR, NIR and fluorescence spectroscopy,

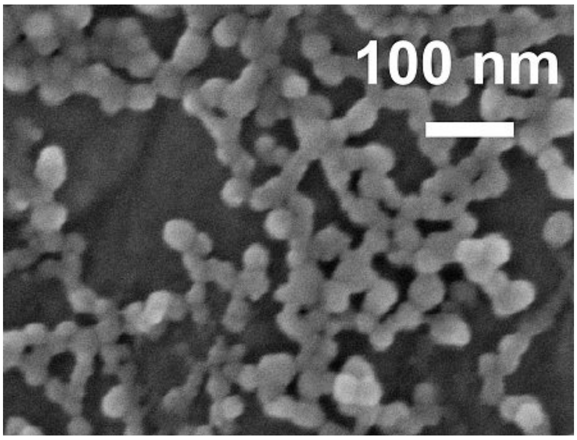

Fig. 5. Scanning electron micrograph of nanoparticles from continuous crystallization in a microreactor system.

PTR-TOF-MS, capillary-inlet MS, process GC and on-line flow cytometry are being used at the ICBC as analytical technologies in this context.

iii) Biocatalysis and biochemical engineering

Catalysis by enzymes or by whole-cell systems provides a way of conducting complex chemical transformations under very mild conditions. Including biocatalytic steps in a process sequence can dramatically improve and/or shorten the synthesis, especially (if not exclusively) where highly functionalized molecules with several stereo centers are involved. Frequent challenges are process control and work-up (downstream processing).

The chemistry curriculum at the ZHAW is unique insofar as it gives students the opportunity to choose between a 'chemistry' and a 'biological chemistry' study profile. While the profiles are not designed to be specializations (graduates of either profile are fully trained applied chemists), graduates with a 'biological chemistry' profile (selected by 30–50% of the students) have additional up-to-date know-how in biochemical engineering, that is, the implementation of chemical processes that make use of enzymes or even organisms to achieve complex chemical transformations with high selectivity under mild conditions, and their integration into multistep reaction sequences.

The following example on the creation of nanoparticles in microreactors illustrates some of our ongoing research on continuous processes (Fig. 5).

Crystallization is a very widely used unit operation that frequently suffers from poor control and reproducibility, and may therefore profit from being carried out in a continuous manner where precipitation conditions are reproducible and controlled. Control of precipitation conditions also opens up an attractive energy-efficient way of producing nanoparticles with narrow size distributions. Among numerous other applications, such particles are of interest in drug delivery of poorly soluble active compounds. Device clogging is, however, an obvious challenge in handling solids in microreactors. The mixing characteristics of different mixing chambers, *e.g.* a valve mixer, are currently being investigated in order to prevent clogging and optimize conditions for reproducible nanoparticle formation.

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[1] cefic (european chemical industry council); Facts and Figures 2010, *www.cefic.org*.

[2] P. T. Anastas, J. C. Warner, 'Green Chemistry: Theory and Practice', Oxford University Press: New York, **1998**.

[3] J. Chenevard, Master Thesis, University of Applied Sciences Western Switzerland, Sion, **2012**.

[4] J. Mutschler, T. Rausis, J.-M. Bourgeois, C. Bastian, D. Zufferey, I. V. Mohrenz, F. Fischer, *Green Chemistry*, **2009**, *11*, 1793.

[5] M. Happe, P. Grand, S. Farquet, S. Aeby, J.-C. Héritier, F. Corthay, E. Mabillard, R. Marti, E. Vanoli, A.-F. Grogg, S. Nussbaum, A. Roduit, F. Tièche, S. Salem, C. Constantin, E. Schmitt, S. Zahno, C. Ellert, A. Habib, J. Wyss, F. Fischer, *Green Chemistry*, **2012**, accepted,10.1039/C2GC35479A. Project video on Youtube: *www.youtube.com/watch?v=0MD2i7ErQKo* or search for: «ECO²BioPro ST».

[6] B. Volesky, 'Sorption and Biosorption', BV Sorbex Inc., Montreal, **2003**.

[7] F. Nussbaum, S. Crelier, 'Effluent treatment: copper biosorption on seaweed/chitosan beads', Poster presented at the XVIIth International Conference on Bioencapsulation, Groningen, Netherlands, September 24-26, **2009**.

[8] C. Vuitel, Bachelor Thesis, University of Applied Sciences Western Switzerland, Sion, **2011**.

[9] F. Nussbaum, R. Dufresne, I. Savoy, A. Schertenleib, C. Bellon, R. Dufresne, S. Crelier. 'Matrices et technologies d'encapsulation pour la production de biosorbants «low-cost»'. Rapport de projet déposé dans le cadre du programme de la réserve stratégique de la HES-SO, **2010**.