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Energy-related Chemical Research at the Universities of Applied Sciences

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Abstract: An overview of current activities in the field of energy-related chemical research at the Swiss Universities of Applied Sciences is presented.

Keywords: Biofuel · Carbon dioxide capture · Luminescent solar concentrator · Microbial fuel cell · Solar heating

Introduction

The growing global energy consumption rate, which has been predicted to double from 13.5 TW in 2001 to 27 TW in 2050, is one of the most important scientific and technical challenges of this century.[1] The majority of the primary energy supply is currently derived from fossil fuels (81% in 2010).[2] Meeting future global energy demands will require a transition from fossil fuels to a more sustainable energy mix. Chemistry plays a key role in this transition by developing new materials for energy conversion and storage, as well as by introducing efficient and energy-saving processing technologies. The Universities of Applied Sciences are contributing to the field of energy-related research through a wide variety of application-oriented projects, some of which are highlighted in the following.

FHNW Muttenz

In recent years, many different ideas to generate fuel from renewable sources were discussed. Regarding biofuel generation, bioethanol is one of the most common renewable fuels worldwide. Large bioethanol plants have been in operation for many years, for instance Südzucker in Zeitz produces 260 million liters of bioethanol per year. However, production of water-free ethanol requires a lot of energy due to the fact that ethanol forms an azeotropic mixture with water. Different thermal separation steps have to be combined to receive almost water-free ethanol.

Hybrid technologies, namely the combination of rectification and pervaporation or vapor permeation are interesting alternatives to commonly used processes. The rectification gives process reliability whereas the membrane process selectively removes water from ethanol.[3] To obtain a concentration of the distillate close to the azeotropic point, a large number of theoretical steps are required, which normally leads to high columns. If height is the limiting factor, an increase of the reflux ratio can also improve the distillate concentration. However, an increase of the reflux ratio also means a higher energy demand for both evaporating and condensing of the distillate. With a sequential membrane unit, a lower reflux ratio and a sufficiently low height of the column can be achieved, concurrently with an increase of installed membrane area. In technical installations however, membranes are regarded as spare parts, which have to be replaced after a period of 1–3 years. Increasing the membrane area saves energy during bioethanol production but increases total costs of ownership.

In this study a 30 mm diameter rectification column and a pervaporation unit (containing 0.02 m² of ceramic or polymer membrane) were used for the energy optimization of the dewatering process (Fig. 1). The system was used for the dehydration of several alcohol–water mixtures. For the bioethanol dehydration a 10% ethanol in water mixture was used, representing a test ratio that is common in bioethanol fermentation production processes. With this mixture, both the rectification and membrane unit was optimized with respect to energy demand and single unit design.

Due to the expected longer lifetime and better thermal stability, ceramic membranes were tested with priority and compared to polymer membranes. In many test runs with different parameters like temperature and flow rate, the membranes were characterized regarding their water flux and solvent purity obtained, measured

Fig. 1. Hybrid process (rectification and pervaporation unit).

by the density.[4] The membrane data obtained were input into a simulation model for the optimization of the hybrid process (rectification and membrane unit). It could be shown by calculation that a very low reflux ratio and few theoretical steps as well as a reasonably high installed membrane area lead to a continuous dewatering process of ethanol with a low energy demand compared to alternative technologies. On-going experiments with different membranes and different feed rates are expected to underline the already achieved results.

HES-SO Sion

Energy research at the Life Technologies Institute in Sion is focused on waste conversion into fuels by biocatalysis and energy efficiency in bioprocessing. The often interdisciplinary research is facilitated through collaborative work with the nearby Systems Engineering Institute, whose activity covers hydropower, photovoltaic, wind energy, smart grids and energy efficiency. Energy research at the institute began with investigations on electricity production from microbial fuel cells. They are thought to be useful to power hand-held electronic devices (Fig. 2), or implanted pace makers and for large-scale applications such as power generation during waste-water treatment. Their application is investigated for industrially relevant microbes such as *Yeast*, *Escherichia coli* and mixed consortia as used in waste-water treatment. A method to assess the productivity of given bioelectrical systems in a step-by-step manner is available for the design of new bioelectrical system variants and optimization.

Fig. 2. Energizing the cellphone with a cube of sugar to run an embedded biofuel cell.

The use of the microbial fuel cell for phosphate recovery from iron phosphate contained in digested sewage sludge is currently under investigation.[5] In this project an up-scale reactor has been constructed and operated. The microbial fuel cell concept also enables the production of bio-hydrogen instead of bio-electricity, which is studied in two on-going projects.[6] The microbial electrolysis cell combines fermentation and standard electrolysis. The voltage needed is reduced by an order of magnitude from 1.22 V to 0.135 V in comparison to standard water electrolysis. The microbial fuel cell investigations also lead to the development of a bio-inspired hydrogen storage battery, whose concept foresees that it accumulates off-peak electric power from biomass, wind, sun and other renewable sources and is released as electricity in peak time.[7] This bio-hydride power storage is potentially also useful for cofactor regeneration in enzymatic redox catalysis. The activity in energy research was recently enriched by the acquisition of two European projects. In the first one, named ORION, the improved methanization of fish and food wastes with a new generation of digester is investigated.[8] The second is the SYNPOL project, in which bacteria are fed with carbon monoxide (Syngas) to produce a biopolyester as well as hydrogen as second product.[9] The biofuel investigations also include enzymatic biodiesel production from micro algae and vegetable oils.[10] Energy efficiency in industrial biotransformation is of importance for products such as biodiesel, lubricants, surfactants and specialty chemicals. In particular the production cost of renewable performance chemicals needs to be lowered to become competitive on the market. For this purpose a microwave barrel reactor was constructed and tested to conduct enzymatic catalysis with reduced energy consumption. The immobilized lipase was not denatured by microwave induction as shown by comparing the results to a reference process in a standard reactor with heat exchanger. Enzymatic reactions with no solvent or only small solvent concentrations are also an approach to reduce energy consumption in industrial production as downstream processing becomes less expensive.

Ecole d'Ingénieurs et d'Architectes de Fribourg

Research on energy-related questions within the Institute Chemical Technologies (ChemTech) is mainly focused on the research axis 'Process Development & Chemical Engineering'. Based on our strong competences in applied and industrial chemistry in teaching and R&D and with the unique equipment of a small pilot plant with reactors up to 600 L, we work on all aspects of optimizing chemical reactions to save resources and design processes using less energy. To do that, we use common process development tools like design of experiment (DoE), quality by design (QbD) and online analytical equipment. Another area of research is advanced scale-up/scale-down methodologies and the use of flow chemistry to optimize, respectively minimize the ecological footprint of chemical processes. Beside the reduction and valorization of waste from industrial processes to save energy, we present here two recent applications from our laboratories using and developing alternative renewable energy sources.

In cooperation with the institute of mechanical engineering we are developing a solar-based heating unit for a distillation plant (Fig. 3). Solar thermal collectors on the roof collect the heat and with in-house developed control engineering applications and automation allows easy and efficient control of the 'solar' distillation plant. By using solar thermal energy we are able to run distillations over several days of very complex and difficult separation problems. This 'solar heating' application has the potential for industrial applications or developing countries. We are developing this concept further for general use of solar thermal energy in chemical production.

In the search for novel and innovative energy sources the institute ChemTech works on the capture and valorization of carbon dioxide. For the selective capture of CO_2, we are developing task-specific ionic liquids (TSIL). These TSIL are based on natural products and show remarkable high loading capacities for CO_2. The carbon dioxide-loaded TSIL can be then directly used in hydrogenation reactions to produce C_1-building blocks like formic acid, formic acid derivatives or methanol. By using hydrogen from solar water splitting or electrolysis, this approach would allow the very efficient production of carbon-neutral fuel for mobility and other applications.

ZHAW Wädenswil

One particular area of research at the Institute of Chemistry and Biological Chemistry focuses on the development of light-management materials, which can for example be used in light-harvesting devices such as luminescent solar concentrators (LSCs). The great potential of LSCs has been known for over 30 years, but low efficiencies and insufficient stability have so far

Fig. 3. Distillation unit heated by solar thermal energy.

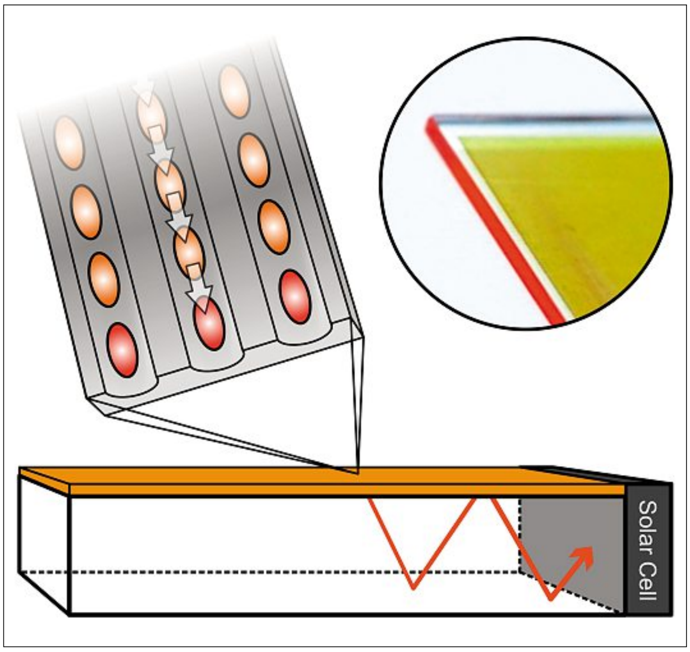

Fig. 4. Luminescent solar concentrator based on a host-guest material as the active component in a thin polymer film on a waveguide. Dye molecules are aligned in the nanochannels of the host and harvest light by a FRET mechanism. Self-absorption of the emitted light is reduced by a well-selected combination of donor dyes (orange) and acceptor dyes (red). Note the edge luminescence shown in the photographic image of a corresponding device (top right).

prevented commercialization.[11] Conventional LSCs consist of a plastic sheet – typically poly(methyl methacrylate) – containing strongly fluorescent organic dyes. Alternative architectures are based on dye/polymer thin films on waveguides.[12] Incident sunlight is absorbed by the fluorescent dye molecules and the subsequently emitted light is partially trapped in the waveguide by total internal reflection. Coupling of LSCs to small edge-mounted solar cells leads to low-cost light-weight photovoltaic devices that work equally well in direct and diffuse light. However, the inevitable overlap between the absorption and emission spectra of the fluorescent dyes leads to strong self-absorption and ultimately to insufficient device performance.[12]

Overcoming the efficiency and stability problems of conventional LSCs requires the development of new fluorescent materials. We are investigating photonic antenna systems based on highly organized host-guest materials with nanochannel-array architectures,[13] including zeolites[14] and more recently also mesoporous silica.[15] The photonic antenna function is based on efficient Förster resonance energy transfer (FRET), which is established by introducing suitable chromophores into the nanochannels of the inorganic host material (Fig. 4). Through a combination of light-absorbing dyes (donors) and small amounts of light-emitting dyes (acceptors), self-absorption can be reduced and the emitted light can be wavelength-matched to the edge-mounted solar cells. The stability of the organic dyes is increased by inclusion into the inorganic host.

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[1] N. S. Lewis, D. G. Nocera, *Proc. Natl. Acad. Sci.* **2006**, *103*, 15729.
[2] Key World Energy Statistics, International Energy Agency, **2012**.
[3] K. Sattler, 'Thermische Trennverfahren: Grundlagen, Auslegung, Apparate', 3. Auflage, Wiley-VCH, **2004**.
[4] D. Mollet, W. Riedl, 'Inlinemessung von Dichte und Brechungsindex bei der Flüssig-flüssig Extraktion', Posterbeitrag, ProcessNet Fachtagung Extraktion, Baden-Baden, **2013**.
[5] F. Fischer, C. Bastian, M. Happe, E. Mabillard, N. Schmidt, *Bioresource Technol.* **2011**, *102*, 5824.
[6] F. Fischer, Projects WEB-Power and Biohydrogène.
[7] F. Fischer, S. Mermoud, G. Diouf, C. Bastian, *J. Appl. Electrochem.* **2012**, *42*, 419.
[8] S. Crelier, *www.project-orion.eu*.
[9] M. Zinn, *www.synpol.org*.
[10] J. Chenevard, F. Fischer, 'Micro algae cultivation and enzymatic biodiesel synthesis', SCG Fall Meeting, September 13, **2012**, Zürich (Poster Award).
[11] M. G. Debije, P. P. C. Verbunt, *Adv. Energy Mater.* **2012**, *2*, 12.
[12] T. Dienel, C. Bauer, I. Dolamic, D. Brühwiler, *Solar Energy* **2010**, *84*, 1366.
[13] D. Brühwiler, G. Calzaferri, T. Torres, J. H. Ramm, N. Gartmann, L.-Q. Dieu, I. Lopez-Duarte, M. V. Martinez-Diaz, *J. Mater. Chem.* **2009**, *19*, 8040.
[14] G. Calzaferri, A. Kunzmann, D. Brühwiler, C. Bauer, Pat. WO2010009560.
[15] N. Gartmann, D. Brühwiler, *Angew. Chem. Int. Ed.* **2009**, *48*, 6354.