Direct synthesis of hydrogen peroxide with CO_2 as solvent in a membrane micro reactor

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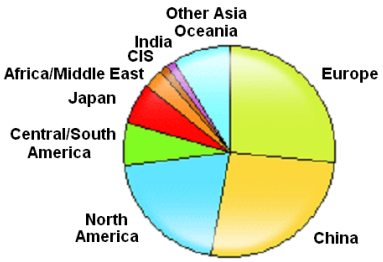
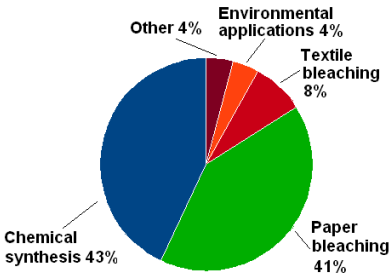
Motivation

World consumption of H_2O_2[3]



H_2O_2 applications in Europe[2]



H_2O_2 annual global consumption is ca. $3 \cdot 10^6$ t/y[1]
Expected growth (just for the HPPO-Process) is ca. $2 \cdot 10^5$ t/y[1]

H_2O_2 advantages:
- ✓Environmentally harmless – the only by–product is water
- ✓Higher activity and selectivity than conventional oxygen

H_2O_2 limitations:
- ✓Expensive – manufacturing price 0.53-0.80 € /kg
- ✓Complicated industrial synthesis – "Anthraquinone Process"

Limitations of the "Anthraquinone Process" :
- ✓Economically viable only for large scale production units (>40 kt/a)
- ✓Expensive and complex solvent system
- ✓Waste of alkyl-anthraquinone during the hydrogenating step due to side reactions

[1] C. Brasse und B. Jaeger, *Elements* 17 (2006) 4-7; [2] J.Fierro et al., *Angew. Chemie* 118 (2006) 7116-7139; [3] S. Schlag et al.„Hydrogen peroxide", *Report, SRI Consulting* (2009)

Objectives

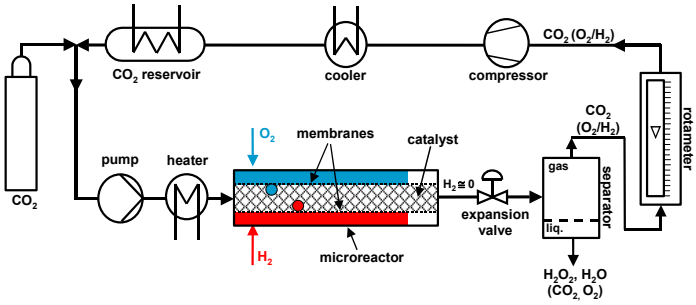
Aim of the project is to develop a compact and efficient continuous process for "on site" production of aqueous hydrogen peroxide solutions, based on the direct oxidation of hydrogen with oxygen in liquid or supercritical carbon dioxide over Pd supported catalysts in a special microstructured double membrane reactor.
The idea is to combine the advantages of the microreaction technology with the benefits of carbon dioxide as a solvent to design an environmentally friendly and efficient process.

Advantages of the microreaction technology
- improved process safety
- enhanced heat- and mass-transfer and reduced limitations on reaction kinetics
- relative simple scale-up (numbering up)

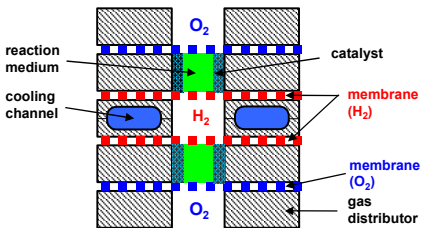
Advantages of CO_2 as a reaction medium
- non toxic, non flamable
- easy separable from the products by simple expansion of the reaction mixture
- enhanced transport properties of the reactants

Experimental set-up

The experimental set-up is schematically represented below. In the first project phase it was put into operation without the implementation of the CO_2 loop, which is planned for a later stage after extensive investigation of the gas phase composition at the exit of the rotameter, in order to meet the exact requirements for the CO_2 compressor.



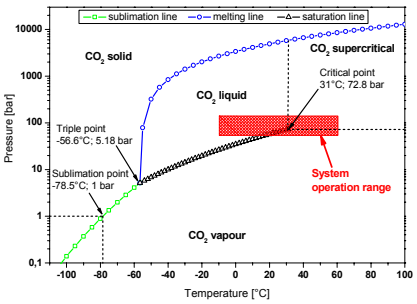
The double membrane micro reactor for the laboratory set-up is currently being developed. At the end of the project a prototype reactor should be built with upscale factor of approx. 10 of the laboratory microreactor. The most likely design of the prototype is to have the membranes facing each other with the microchannels in between, giving relatively easy opportunity for numbering up by preparing stacks with optional built in cooling.



Possible membrane materials
planar porous ceramics
polymer membranes
micro sieves

Catalysts
Supported Pd or Pd doped with a second precious metal in the form of wall coating or a packed bed

Operating conditions and principle



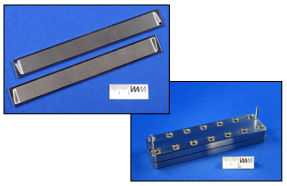
Operation range of the laboratory system
- Temperature: -10 to 60 °C
- Pressure: 60 to 180 bar
- Flow: 0,3 – 1,2 L h^{-1}
- Pd amount: ca. 100 mg
- Prototype reactor – upscale factor 10 compared to the laboratory microreactor

Liquid CO_2 - contactor principle
Bubble free supply of the reactants through the membranes.
Important membrane parameters in this case are the pore size and distribution, membrane thickness and wetting properties (hydrophobicity)

Supercritical CO_2 - mixer principle
Direct mixing of the reactants in the supercritical phase. In this case the most important parameters are pressure and temperature, in order to keep the mixture supercritical

Catalyst screening

Aim of these experiments is to identify the most suitable catalyst for the direct synthesis reaction in an earlier project phase. A number of test micro reactors were prepared, each of them representing a separate catalyst in the form of wall coating of the microchannels. 1%Pd/Al_2O_3 and 1%Pd/TiO_2 were the first chosen catalyst combinations. The activity and selectivity of these catalysts will be investigated for different experimental conditions – type of solvent (liquid or supercritical CO_2), pressure, temperature, system flow, stoichiometry etc.



Test reactors:
Channel geometry (l, w, h): 150 x 0,5 x 0,6 mm
Number of channels per plate: 20
After coating two plates are welded together
Maximal pressure: 150 bar;
Maximal temperature: 50°C
Volume flow: 5 to 20 ml min^{-1}

Catalyst coating method – waschcoating:

Step 1: Preparation of the catalyst powder by impregnation of the support material (TiO_2, Al_2O_3) with the active component (Pd: 0,5; 1 or 2 % w/w) and calcination

Step 2: Preparation of a suspension of the catalyst powder with addition of a binder and other additives

Step 3: Coating of the micro channels

Step 4: Drying and calcination of the coatings either in air or nitrogen atmosphere

The thickness of one coating layer is 20 - 25µm and can be varied through multiple coatings

Project partners

- ✓ IMM Mainz GmbH – Ulrich Krtschil, Christian Hofmann, Volker Hessel
- ✓ Microinnova Engineering GmbH – Dirk Kirschneck, Walter Linhart,