Process development for small-scale direct synthesis of hydrogen peroxide in a catalytic membrane contactor

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Motivation

Hydrogen peroxide is an oxidizing agent widely used in many industrial areas:
- ✓Chemical industry - production of peroxy compounds
- ✓Textile and paper industry – bleaching agent
- ✓Environmental protection – detoxification of waste waters and exhaust gases

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

H_2O_2 disadvantages:
- ✓Expensive – manufacturing price 0.53-0.80 EUR/kg
- ✓Complicated synthesis – "Anthraquinone Process"

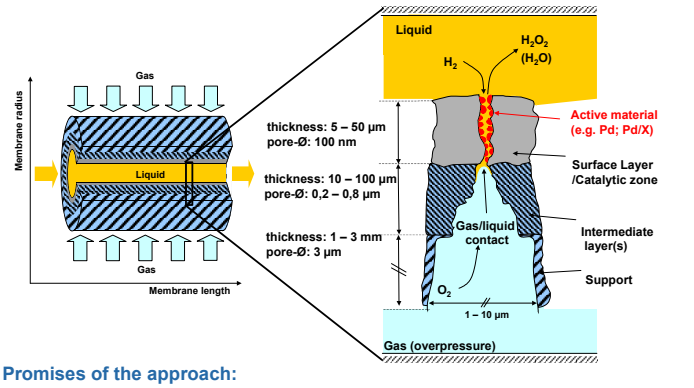
Limitations of the "Anthraquinone Process" :
- ✓Economically viable only for large scale production units (>40 kt/a)
- ✓Expensive and complex solvent system
- ✓Waste of alkyl-anthraquinone during the hydrogenating step due to side reactions

Objectives

The aim of the project is to develop a compact system for on-site direct synthesis of hydrogen peroxide from O_2 and H_2 on small scale. An important issue is the safety of the continuous process, guaranteed by the use of a catalytic membrane contactor operating on the principle of the "catalytic diffuser".

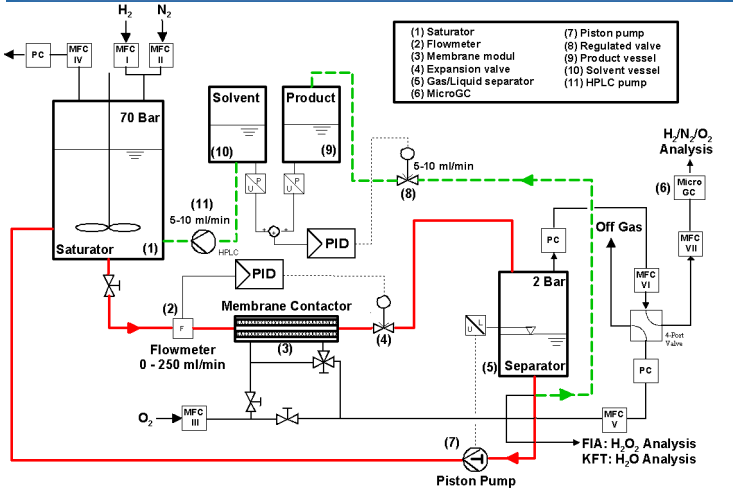
"Catalytic diffuser" concept

The so called "catlytic diffusor" represents a tubular ceramic membrane with asymetric structure (prepared from or project partners HITK, Hermsdorf) and highly dispersed catalytic nanoparticles deposited preferably on the inside of the membrane channel in the membrane layer with the finest pores. The liquid is fed from the innerside of the membrane tube and the gas is fed in overpressure from the coarse porous membrane side.



Promises of the approach:
- ✓Separated supply of H_2 and O_2 – safe operation
- ✓Highly dispersed active material, therefore high active surface area per m^2 of membrane area and per gram of catalyst – high productivity
- ✓Moderate limitation by mass transfer due to thin catalytic zone
- ✓Relatively easy scale-up by exploiting multi-channel tubes
- ✓Well suited for on-site production for direct use in small scale applications

Experimental set-up for continuous operation



Mathematical model of the membrane contactor

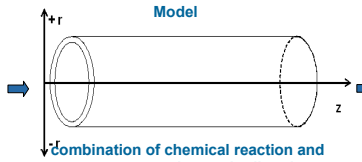
First experiments with single channel catalytic membranes lead to very low H_2O_2 formation in the order of $3 \cdot 10^{-4}$ mol L^{-1} with approx. 9% selectivity. In order to understand the reasons for the poor performance of the membrane contactor a mathematical model, describing the combination of chemical reaction and mass transport within the membrane channel, was set up.

Input Parameter

Reaction conditions: T, P_L, P_G, $x(H_2)$, $x(O_2)$, $x(N_2)$, F_L, F_G, m(Pd), type of solvent

Membrane geometry: l, r, ε, τ, dr

Henry coeffitients, diffusion coefficients, densities

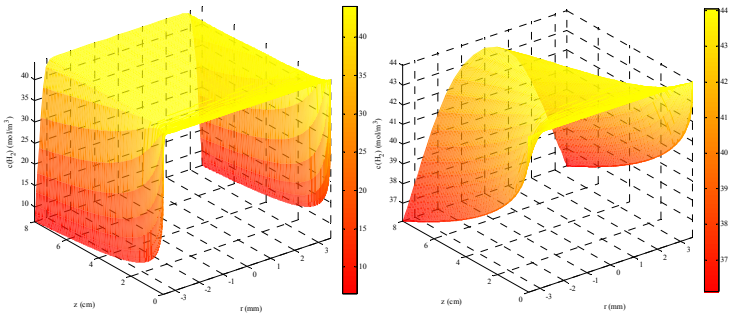


Output parameter

Time and location dependent concentration profiles in the membrane channel (z direction) and in the liquid filled membrane layer (r direction) – $C(H_2)$, $C(O_2)$, $C(H_2O)$, $C(H_2O_2)$

First simulations indicated a crucial influence of the type of flow in the membrane channel on the performance of the membrane contactor. The concentration of the limiting component H_2 was the output parameter of interest.

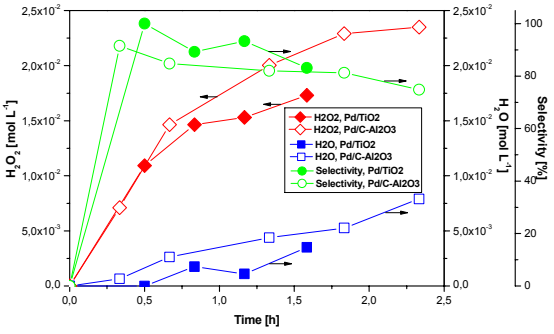
$c(H_2)$ – empty channel | $c(H_2)$ – channel filled with 0,5 mm glass beads



Calculated H_2 concentration profiles show highly limited H_2 transport only by diffusion from the center of the channel to the catalytic zone (channel wall) in the conditions of laminar flow, normally observed in an empty membrane channel. As a concequence almost the whole amount H_2 exits the membrane unreacted (s. graph above, left side). Filling the membrane channel with inert glass beads to accelerate radial mixing led to completely different concentration profile and much higher H_2 utilisation (s. graph above, right side).

H_2O_2 direct synthesis with catalytic membranes

Single channel (d_{out}= 1 cm, d_{in} = 0,7 cm, l = 10 cm) catalytic membranes were tested for the direct synthesis of hydrogen peroxide. The experiments were performed in single pass mode with methanol as a solvent and membrane channels filled with 0,5 mm inert glass beads.



Catalytic membrane	Experimental conditions	Activity [g_{H2O2} g_{Pd}^{-1} h^{-1}]	Activity [g_{H2O2} m^{-2} h^{-1}]	Selectivity [%]
Pd/TiO_2-7	MeOH + 15 mg/L NaBr + 0,03 mol/L H_2SO_4; P_{Fl} = 50 bar; H_2/N_2 = 30/70; $C(H_2)$ = 0,069 mol L^{-1}; $P_G(O_2)$ = 54 bar; m(Pd) = 8,4 and 6,9 mg; F = 13,5 and 8,0 ml/min	57,46	207,74	83,1
Pd/C-Al_2O_3		55,42	217,94	74,8

Summary

Accomplished project goals
- ✓Completed experimental set-up for continuous operation
- ✓Proved long-term operational stability of the continuous system with single channel membranes
- ✓Developed a reliable system and method for continuous H_2O_2 detection
- ✓Developed a suitable catalyst coating procedure leading to active catalysts
- ✓Identified promising catalytic systems (Pd/C-Al_2O_3, Pd/TiO_2)

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