ELSEVIER

Numerical analysis of mass transport effects on the performance of a tubular catalytic membrane contactor for direct synthesis of hydrogen peroxide

Manuel Selinsek [a,*], Aneta Pashkova [b], Roland Dittmeyer [a]

[a] Karlsruhe Institute of Technology, Institute for Micro Process Engineering (IMVT), Hermann-von-Helmholtz-Platz 1, D 76344 Eggenstein-Leopoldshafen, Germany
[b] DECHEMA-Forschungsinstitut, Theodor-Heuss-Allee 25, D-60486 Frankfurt am Main, Germany

ABSTRACT

Despite intensive research carried out by academia and industry over the past decades, the liquid phase direct hydrogen peroxide synthesis still faces a lot of challenges including safety, selectivity and productivity of the reaction. One facet of this multiphase reaction is the mass transport of the gaseous reactants, hydrogen and oxygen, in the liquid phase and inside of the catalyst. However, this has not been receiving much attention although, in many of the experiments reported in literature it seems to have affected to a large extent the results obtained. In this paper we report an analysis of performance data from a catalytic membrane reactor system published by Pashkova et al. in 2010 [1]. A rigorous two-dimensional model based on ANSYS Fluent was adopted to study the effects of an inert packing installed in the membrane reactor. The simulation results reveal a massive influence of mass transport limitation on the performance of the experimental system and also indicate significant potential for optimization of productivity and selectivity by adopting micro process technology combined with membranes for reactant dosage.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Hydrogen peroxide is a powerful, clean and very versatile oxidant with water being the only oxidation byproduct. The worldwide production exceeds 2.2 Mt/a with an annual growth rate prediction of 4% [2,3]. Most commonly hydrogen peroxide is used as a bleaching agent in the pulp/paper industry or as a disinfectant in wastewater treatment. Currently hydrogen peroxide is produced by the anthraquinone auto-oxidation (AO) process, where the product is formed via a two-step process on an organic carrier molecule. The AO process is only viable for large scale production greater than 40 kt/a [3], which is accompanied by high transportation costs to the consumer. The liquid phase direct synthesis of hydrogen peroxide offers the advantage that hydrogen peroxide is directly formed from its elements, hydrogen and oxygen, and the only byproduct is water. This technology would enable small scale on-site production, thus reducing transportation costs and expanding the market even further by making hydrogen peroxide available for innovative oxidation processes.

However, the direct synthesis of hydrogen peroxide still faces a lot of challenges, which hinders the process from being commercially applicable. One main problem is to achieve high selectivity [4]. Hydrogen peroxide is a thermodynamically unfavoured intermediate of the considered reaction network, which includes parallel water formation and consecutive decomposition and hydrogenation of hydrogen peroxide besides the actual synthesis itself [5]. In addition, the materials which catalyze the synthesis are also active for the unwanted side reactions. Another major drawback is that hydrogen and oxygen form an explosive gas mixture over a wide range of concentrations. This has to be avoided by dilution of the gases, which leads to low concentrations in the liquid phase and thereby reduces the overall rate of hydrogen peroxide production [4,6].

Especially at these low concentrations mass transfer of the gaseous reactants in the liquid phase plays a huge role. The gas–liquid mass transfer is limited by the solubility of hydrogen and oxygen in the solvent, whereas the liquid–liquid, liquid–solid and the mass-transfer inside the porous catalyst is limited by slow liquid phase diffusion [7–11]. All these effects have to be taken into account when assessing the performance of different catalysts and reactor concepts or when trying to obtain further inside on the reaction mechanism and kinetics. The mass transfer influences the

* Corresponding author. Tel.: +49 721 608 25326.
  E-mail address: manuel.selinsek@kit.edu (M. Selinsek).

reactant concentrations in the liquid phase and at the active sites and thereby not only the overall production rate, but also the selectivity by e.g. determining the hydrogen to oxygen ratio inside the catalyst.

Membrane reactors are promising systems to overcome the challenges mentioned above [1,12–14]. The membrane technology enables a separated dosage of the reactant gases into the liquid reaction medium, for example by having one reactant dissolved in the liquid feed, while the other reactant is fed over the membrane. This allows the usage of high partial pressures without risking the formation of an explosive gas mixture. So far the sometimes delicate handling of the membranes as well as mass transfer limitations have hindered these types of reactors from being commercially applicable [3]. Recently microreactors gained interest for the direct synthesis of hydrogen peroxide [15–18]. They offer the possibility to operate within the explosive regime without causing safety issues [16,17,19]. This also allows the usage of higher reactant pressures resulting in higher liquid concentrations and higher production rates. Another advantage is that microreactors show excellent mass transfer properties due to the small inner dimensions. Hence microreactors appear to be very attractive to overcome the challenges in the direct synthesis of hydrogen peroxide.

In the present work the influence of the mass transfer on the direct synthesis of hydrogen peroxide has been examined. A two-dimensional model of the catalytic membrane reactor for ANSYS Fluent was adopted. To prove the reliability of the model the simulations are compared to experimental data generated by Pashkova et al. [1,20].

2. Materials and methods

2.1. Experimental setup of the membrane contactor

Pashkova et al. concluded from their experiments that the performance of their membrane contactor for the liquid phase direct synthesis of hydrogen peroxide strongly depends on the diffusive transport of hydrogen to the catalytic zone [1]. They showed this by filling their membrane reactor tube with inert glass beads to enhance the radial dispersion of hydrogen, which led to a ca. 100 fold increase of produced hydrogen peroxide.

A single channel tubular membrane reactor with a fine porous, catalyst coated layer at the inside was used in their experiments (inner diameter = 7 mm, length = 100 mm, thickness of fine porous layer = ~0.04 mm, mean pore diameter of fine porous layer = ~100 nm, porosity of fine porous layer = ~0.3). The thickness of the catalyst coating was determined by electron probe micro analysis, the mean pore diameter and the porosity of the layer were determined by mercury porosimetry [1,20]. The liquid solvent, water or methanol, was saturated with a hydrogen/nitrogen mix in a stirred tank and then introduced in the tubular channel. Oxygen was dissolved in the solvent over the length of the reactor via the gas phase outside of the porous membrane. The reaction takes place in the fine porous, catalytic layer. The reactor principle is schematically shown in Fig. 1.

2.2. Two-dimensional model of the membrane reactor

The two-dimensional simulations of the membrane reactor have been carried out using the software ANSYS Fluent, which is a tool for solving fluid flow problems. This software is based on the numerical solution of the Navier-Stokes equations for a discretized geometry. The reactor geometry used by Pashkova et al. [1] was drawn with a CAD software incorporated in the ANSYS package. Because of the axisymmetric nature of the problem a two-dimensional model was selected. The simulated geometry consists of four zones: one zone

Table 1
Henry constants for the gaseous components at 298.15 K taken from the DETHERM database [21].

Solute	Solvent	Henry constant (bar mol mol^{-1})
H_2	H_2O	6.789×10^4
	CH_3OH	5.249×10^3
O_2	H_2O	4.800×10^4
	CH_3OH	2.471×10^3
N_2	H_2O	8.762×10^4
	CH_3OH	3.923×10^3

each for the inlet at the entrance and the outlet at the exit of the reactor to prevent possible influences of the flow regime formation, a bulk zone for the channel optionally filled with inert packing and a zone for the fine porous catalytic layer inside of the membrane at the edge of the bulk zone. It was assumed that the gas liquid interface is established at the transition from the fine porous zone and the coarse part of the membrane due to the capillary forces. Therefore, only the fine porous zone was implemented in the model geometry. A scheme of the geometry as well as its dimensions used for the simulations is shown in Fig. 2.

For this geometry a mesh was generated containing 11750 quadratic cells for the CFD calculations. The cell height was lessened from the symmetry axis to the top side to prevent high aspect ratios of the cell dimensions at the transition from the bulk zone to the catalytic membrane. By refining the grid to 140,000 cells it was checked that the solution obtained by Fluent is independent of the cell dimensions.

At the inlet of the reactor it was assumed that the solvent is saturated with hydrogen and nitrogen according to the conditions present in the saturator. For the membrane, it was assumed that the solvent is saturated with oxygen at the gas liquid interface. The saturation concentrations of hydrogen, nitrogen and oxygen were calculated after Henry's law (Eq. (1), see Table 1 for the used constants). The oxygen source was described according to Fick's first law, where the flux of oxygen f_{O_2} into the liquid phase is driven by the gradient between the saturation concentration c_i^* at the interface and the cell concentration $c_{O_2,\text{cell}}$ calculated by ANSYS Fluent (Eq. (2)). The source term was implemented in the cell layer at the top side of the catalytic membrane zone.

$$x_i^* = \frac{p_i}{H_i} \tag{1}$$

$$f_{O_2} = D_{O_2,j} \frac{(c_{O_2}^* - c_{O_2,\text{cell}})}{\Delta y} \tag{2}$$

with: saturation mole fraction x_i^*, partial pressure p_i, Henry constant H_i, diffusion coefficient $D_{i,j}$, half of the cell height Δy.

The plug flow formation through the glass bead bed and the absence of convective flow in the fine porous membrane zone was implemented in the simulation with the porous body model of ANSYS Fluent. This model describes the flow regime and pressure loss in a porous zone. For this model an inertial loss and a viscous loss term (reciprocal permeability α) have to be defined. For the glass bead bed the required coefficients can be directly determined by equation 3–4 implemented in Fluent. Given that the recommended equations strictly apply only for packed beds, a correlation was used to predict a packed bed equivalent particle diameter d_p corresponding to the mean pore diameter d_c for the fine porous membrane zone (Eq. (5)) [22]. The void fraction of the glass bead bed was assumed to be 0.45, a typical value for randomly packed beds.

$$\alpha = \frac{d_p^2}{150} \frac{\varepsilon^3}{(1-\varepsilon)^2} \tag{3}$$