Towards a new membrane micro reactor system for direct synthesis of hydrogen peroxide

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ABSTRACT

The approach of producing hydrogen peroxide (H_2O_2) by direct catalyzed reaction of H_2 and O_2 has been extensively studied over the past decades. The process offers the potential to establish a "green" alternative to the conventional large-scale anthraquinone process. However, the implementation of this reaction still faces major hurdles including safety, selectivity and productivity of the reaction. In this work, we report results on the development of a novel intensified suspension-flow membrane micro reactor system for direct synthesis of hydrogen peroxide as well as on a related flexible micro reactor system for transfer hydrogenation which served as a starting point. In the new reactor system for H_2O_2 direct synthesis safety issues are greatly reduced by the introduction of a membrane to separate the gaseous reactants. Furthermore productivity is maximized by increased mass transfer in micro channels and constant reactant feeding over the length of the reactor. Finally, the selectivity can be optimized by controlling the reactant distribution in the liquid phase. A rigorous two-dimensional single-phase model based on ANSYS Fluent was adopted to study the influence of the design on the reaction. This model had already been validated in a previous study. By expanding the model to describe the multiphase phenomena we were able to get further insight on the behavior of the overall system.

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1. Introduction

Hydrogen peroxide is a powerful oxidant and has a "green" nature since water is its only oxidation byproduct. Commercially it is mostly used as a bleaching agent, disinfectant or in waste water treatment. Currently it is almost exclusively manufactured by the anthraquinone auto-oxidation (AO) process [1]. Due to the complexity of the AO process its economic viability is only given for large scale production [2]. This results in the necessity of transporting concentrated H_2O_2 over long distances, which substantially increases the price of the product. There are several alternative routes of producing hydrogen peroxide, e.g. via electrochemical synthesis [3]. But the direct synthesis in the liquid phase is the most straight forward approach since in theory it is exceptionally easy, by just combining one molecule of hydrogen and one of oxygen (Fig. 1).

However, even though the reaction was presented as early as 1913 (application date of patent) [4], it is still not in commer-

cial production. Serna et al. [5] found ca. 70 patents on the direct synthesis filed between 2004 and 2013, but still no example for successful commercialization was reported, though some examples of attempts in that direction are cited. Besides the problem of economics of a new process versus an established one there are several challenges in this seemingly trivial reaction. Hydrogen peroxide is an unfavored reaction intermediate and the competing product water is much more stable. The catalysts enabling the target reaction also catalyze the consecutive hydrogenation of H_2O_2 and the parallel reaction to water. This led to an intensive research on appropriate catalytic materials, which is still ongoing. Mainly noble metals, such as palladium, platinum and gold, or combinations of these mostly supported on alumina, silica or carbon were studied [3]. Palladium seems to be the most promising active metal especially in combination with gold as reviewed in Refs. [6,7].

Besides the problem of selectivity and activity, the main issue with the reaction is the ability of hydrogen and oxygen to form explosive gas mixtures over a wide concentration range. Gas dilution is necessary in order to avoid this. As a consequence, the resulting low partial pressures limit the amount of reactants in the liquid solvent, where the reaction takes place. Thereby conventional multiphase reactor concepts allow only small space time
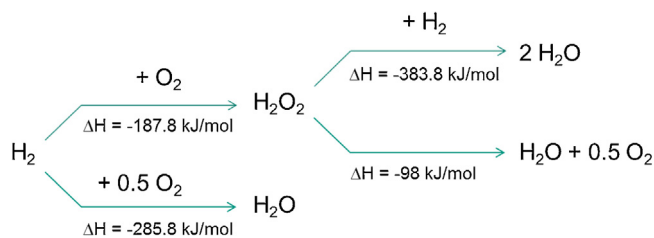
Fig. 1. Reaction scheme of the hydrogen/oxygen/hydrogen peroxide system.

yield, which challenges the process economics. Membrane reactors allow the use of pure reactant gases by spatially separating them and also to constantly feed them over the length of a reaction channel [8,9]. However, there are several challenges tied to this approach as well [6]. One point is the limited mass transport rate through the membranes, which in turn affects the effective concentration and thus the reaction rate. Furthermore, when introducing one of the gases separately via a membrane it is generally difficult to avoid areas with unfavorable stoichiometry. Placement of catalyst inside the membranes has its limitations as well, e.g., the local concentration will be strongly affected by the gas transport, again leading to a deviation of the H_2/O_2 concentration ratio from the desired value. The use of Pd-Ag-alloy-membranes, which could act simultaneously as a catalyst and for hydrogen dosage, has been reported [10], but not found to meet criteria for successful application [6].

Micro reactors, which are known to have excellent heat and mass transfer performance, have also been used in the direct synthesis of hydrogen peroxide [11–16]. One of the points in using micro structured reactors is the fast mass transfer, another one the safety consideration, since the propagation of an explosion can be hindered by narrow channels [17]. Problems with this approach include the difficulty of catalyst integration in micro packed bed reactors, e.g., achieving uniform catalyst distribution within a channel and among multiple channels, and the pressure drop associated with the use of small catalyst particles. And while the feasibility of performing the reaction with good yield in multiphase systems has been shown in laboratory scale, i.e., with a small number of parallel channels, a successful scale-up has not yet been reported and is also not expected for some of the devices applied. It has been shown though, that scale-up is possible in micro reactors, given the correct strategy [18]. In principle the combination of a membrane reactor with the ability to perform the reaction in single-phase mode and micro reaction technology, characterized by an intense mass transport rate should be feasible. Hence we aim at exactly such a combination in a novel system for the direct synthesis of hydrogen peroxide.

2. Materials and methods

2.1. Suspension flow catalysis in curvilinear micro channels

2.1.1. Reactor system and micro channel designs for continuous-flow suspension catalysis

The new reactor design concept proposed here for hydrogen peroxide synthesis builds up on the design of an intensified reactor system for continuous-flow suspension catalysis developed in the EU-FP7-Project F^3-factory [19]. The main benefit of the reactor system is its ability to perform liquid-phase reactions on a heterogeneous catalyst in form of suspended particles in the reaction liquid with high reaction rate due to fast liquid-solid mass transfer and high flexibility regarding the catalyst. The lab module is composed of top and bottom cover plates with an exchangeable micro structured plate in between (Fig. 2).

The micro channel plate has a cooling side and a reaction side. Three independent zones on the cooling side allow for fast heating at the entry, stable temperature over the length of the reaction channel and fast quenching at the exit. The reaction side consists of a curvilinear micro channel for the liquid phase reaction. The micro channel shape was designed to make use of Dean vortices (described below) in order to enhance transversal mass transfer in the liquid phase and to prevent sedimentation of the suspended catalyst particles.

The fluid flow in curvilinear channels experiences centrifugal acceleration directed radially outward leading to the formation of counter rotating vortices. In literature this phenomenon has been proven experimentally by optical analysis of fluid flow in convoluted channels [20] and by studies on the mixing performance in curvilinear channels [21]. In theory the effect of curvature on fluid flow is described by the dimensionless Dean number (De) which is given by [22–24]:

$$De = Re\sqrt{\frac{D_{\text{hyd.}}}{R_c}} \tag{1}$$

The Dean number is a product of the Reynolds number Re and a geometrical factor, which is given by the relation of hydraulic diameter $D_{\text{hyd.}}$ and curvature radius R_c. Three different micro channel shapes (see Fig. 2) were manufactured to study this phenomenon. The geometric details of the channels as well as calculated Reynolds and Dean numbers for various flow rates are listed in Table 1.

2.1.2. Experimental setup

The experimental setup to investigate the fluid flow, sedimentation of particles and reaction performance in micro channels consisted of two liquid feed streams that were pumped from stirred vessels to the micro reactor using HPLC pumps (Knauer Smartline 100 equipped with 10 mL heads). At the reactor entrance both fluids are mixed in a micro mixer before entering the micro channel. Pressure and temperature was measured in the two inlet streams as well as the outlet stream. On the cooling side of the reactor one thermostat was connected for the reactor heating. At the exit of the reactor a manual back pressure membrane valve was installed in order to control the operating pressure beyond ambient.

2.1.3. Suspension-flow and reaction experiments

In these experiments a commercially available 1 wt.-% palladium on carbon catalyst (Johnson Matthey, Ref. no: 139962) was used. The catalyst was sieved with a mesh width of 50 μm to ensure unobstructed flow of particles through the smallest orifices of the flow path (entrance of micro mixer at reactor entry: 200×200 μm). The particle size distribution was measured by static laser diffraction using a Beckmann Coulter LS230. A d90 (90 wt.-% of the particles have a smaller diameter) of 33 μm was found and a maximum size of 85 μm was found by microscopic investigation.

The behavior of the suspension flow regarding particle sedimentation, mixer blocking and particle trapping was investigated by pumping a suspension consisting of the Pd/C catalyst and isopropanol through the different reaction channels. For visual observation a transparent PMMA top cover for the reactor was used (Fig. 3).

As a test reaction the transfer hydrogenation of 6-nitroquinoline to 6-aminoquinoline was chosen (reaction equation (r1)). In this experiment two feed solutions were prepared, one containing 1 L tetrahydrofuran, 66.7 g 6-nitroquinoline and 123.3 g formic acid and the other one containing 1 L tetrahydrofuran, 20 g sieved Pd/C catalyst and 581.1 g triethylamine. The reactor was heated to 60 °C, and the reaction pressure was set to 10 bar using the backpressure valve.