A NOVEL MICRO MEMBRANE REACTOR FOR CONTINUOUS DIRECT SYNTHESIS OF HYDROGEN PEROXIDE

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Abstract

The application of the direct synthesis of hydrogen peroxide from hydrogen and oxygen still faces major challenges including selectivity, productivity and safety. A novel reactor combining the benefits of membranes and micro channels has been developed to address these problems on a technical level. Membranes enable a separated introduction of the reactants in the liquid reaction media, which circumvents the necessity of a dilution to prevent explosive gas mixtures. Micro channels are used for the liquid phase to enhance the mass transfer through short diffusion pathways. The development was supported by 2D and 3D single and two-phase CFD simulations with ANSYS Fluent to study the feasibility of a system of this kind. A flexible laboratory reactor capable of performing the reaction at high pressures was designed and built based on these results. In a first set of experiments the concept of this novel reaction system was proven by performing the direct synthesis with undilute reactants at atmospheric pressure.

Keywords

ISCRE 24, hydrogen peroxide, direct synthesis, mass transfer, membrane, micro reactor.

Introduction

The direct synthesis of hydrogen peroxide (H₂O₂) from hydrogen (H₂) and oxygen (O₂) potentially is a green alternative to the conventional anthraquinone process. However, the application of this reaction faces major challenges. The catalysts, mainly supported palladium, also catalyze the consecutive and parallel formation of water (Figure 1). Furthermore the productivity is limited by slow liquid phase diffusion and low solubility of H₂ and O₂ in the liquid reaction media. The latter is even further lowered due to the necessity of a gas dilution to prevent the formation of explosive gas mixtures. Due to this fact conventional reactor technology, such as fixed bed, trickle bed or bubble column, achieved only low space time yields (Dittmeyer et al., 2015). Micro reactors are able to safely operate within explosive regimes but scale up has not been demonstrated. Membrane reactors offer improved safety by spatially separating the gaseous reactants but suffer from additional mass transfer resistance in the membrane (Selinsek et al., 2015). The question evolved if it’s possible to combine the benefits of micro and membrane reactors while avoiding their disadvantages to form an advanced reaction system.

Figure 1. Reaction scheme in the hydrogen/oxygen/hydrogen peroxide system.

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Results

The novel reactor system is based on the idea of continuously refeeding the separated gaseous reactants through a membrane into a micro channel containing the liquid solvent and the catalyst. This way undiluted high partial pressure reactants can be utilized to increase the limiting liquid phase concentrations, which are further maximized due to the enhanced mass transfer in the micro channel. The influence of mass transfer on the reaction in continuous systems was studied with CFD simulations by adopting a model to describe the dissolution of the gases in the liquid phase based on the film theory and reaction kinetics from the literature to ANSYS Fluent. The simulations have shown that an alternating dosage of the reactants into the liquid phase is superior to an opposed dosage in terms of controlling the ratio between hydrogen and oxygen available for the reaction (Figure 2). This also leads to an increased conversion and selectivity for the alternating case.

Going towards a real system the influence of channel dimensions and dosage lengths were studied. It was shown that a reactor of this kind is able to ensure a steady production of hydrogen peroxide over the length of the micro channel while maintaining high selectivity (Figure 3). Furthermore the maximum achievable hydrogen peroxide concentration in this system is only limited by reaction kinetics, hence the dynamic equilibrium of synthesis and consecutive hydrogenation and decomposition.

Based on the simulation results a first generation micro membrane reactor for laboratory usage was designed and manufactured (Figure 3). A meander-like micro channel plate is used for the flow of the liquid and a plate capable of holding flexible PTFE membranes is then attached on top of it. The micro channel switches the sides beneath two gas channels for the reactants to realize the alternating dosage. The number of alternations as well as the dosage length, channel height, and overall length of the micro channel can then be easily adjusted by changing its shape.

Figure 2. Comparison of the $H_2/O_2$-ratio of an opposed and alternating reactant dosage (empty space: ratio > 2).

Figure 2. Illustration of the new micro membrane reactor.

The production of hydrogen peroxide was observed in an experiment using undiluted reactants at ambient pressure using a commercially available 5 wt.-% Pd/C catalyst in a suspension with water as continuous liquid phase.

Conclusion

A novel micro membrane reactor was developed and manufactured supported by CFD simulations. In theory the system is able to produce high $H_2O_2$ concentrations while maintaining high selectivity by controlling the $H_2/O_2$-ratio in the liquid phase and continuously refeeding the reactants. The concept was proven by successfully performing the reaction at ambient pressure. Further experimental exploration and validation of this system is subject to ongoing studies.

References
