

# Design and optimization of a catalytic membrane reactor for the direct synthesis of propylene oxide



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## HIGHLIGHTS

- Membrane reactor design for propylene oxide direct synthesis in liquid phase.
- Numerical simulation for describing the reactor concept.
- In situ combination of two consecutive reactions (hydrogen peroxide synthesis and propylene epoxidation).
- Optimization of the membrane reactor main properties.
- Scaling up of the membrane reactor.

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## ABSTRACT

Using numerical simulations, a new membrane reactor is proposed for the direct synthesis of propylene oxide (PO) in liquid phase. The reactor is a combination of two consecutive catalytic reactor units, one for the hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) synthesis on a Pd/SiO<sub>2</sub> catalytic membrane layer, and the second for the conversion of hydrogen peroxide with propylene (C<sub>3</sub>H<sub>6</sub>) to PO on a titanium silicalite-1 (TS-1) catalytic layer. The membrane reactor is described numerically by a set of kinetic-diffusion mass balance equations. The optimization of the reactor design is achieved by determining membrane pore size, thickness and gas pressures which provide conversion and selectivity performance comparable to the industrial requirements. An optimal pore size of 0.2–0.4 μm was found for the Pd/SiO<sub>2</sub> membrane layer. The results show that a Pd/SiO<sub>2</sub> membrane thickness of 250 μm and a TS-1 layer of 100 μm are necessary to ensure conversion and selectivity performance of the catalytic membrane reactor comparable to the industrial ones. Calculated these optimized dimensions of the membrane reactor, a total membrane area of 84,000 m<sup>2</sup> is required for the production of 300 kton/year of propylene oxide.

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## 1. Introduction

Propylene oxide (PO) is an important compound due to its versatility in the chemical industry. Since the main traditional processes for PO production are becoming less and less attractive due to economic and environmental concerns (Nijhuis et al., 2006), possible alternatives have been searched in the last decades. The successful implementation of a new process on a large scale lies on its capacity to provide safety, economic, environmental and performance benefits (Cavani and Teles, 2009). The first step towards meeting industrial requirements (Cavani, 2010;

Sinha et al., 2004) for alternative PO production routes has been achieved with the discovery of titanium silicalite-1 catalyst (Tar-amasso et al., 1983). A successful application of this zeolitic material is achieved in the HPPO process, where the epoxidation of propylene with H<sub>2</sub>O<sub>2</sub> leads to PO and water formation. As a result, two large scale plants are currently operating in Belgium and Thailand with a capacity of 300 and 390 kton/year of PO, respectively (Bassler and Weidenbach, 2010; The Dow Chemical Company, 2014). However, the high cost of H<sub>2</sub>O<sub>2</sub> production for a large part determines the cost of the PO synthesis process (Huang and Haruta, 2011). Therefore, the direct synthesis of propylene oxide from hydrogen, oxygen and propylene was proposed as a green and economically advantageous alternative (Monnier, 2001). Two main streams have been distinguished in the research approach: gas vs liquid phase reaction. The gas phase reaction is mainly

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focused on the bi-functional Au–titanium based catalyst (i.e.,  $\text{TiO}_2$ ,  $\text{Ti/SiO}_2$  and TS-1) (Nijhuis et al., 2005, 2010; Yap et al., 2004; Bravo-Suárez et al., 2008). Despite the high PO selectivity of the Au–Ti catalyst, several limitations such as low propylene conversion and hydrogen efficiency, safety concerns and catalyst productivity make the gas phase PO synthesis still far from being operated on a large scale (Sinha et al., 2004). The second option is the liquid phase PO synthesis on Pd or Pd–Pt/TS-1 catalyst (Laufer, 1999; Meiers and Hölderich, 1999; Jenzer et al., 2001). The reaction occurs in two steps where  $\text{H}_2\text{O}_2$  is first in situ generated on Pd particles and then utilized on titanium silicalite-1 catalyst. Several limitations are encountered in the direct PO liquid phase synthesis. The explosive nature of the reactants, the instability of  $\text{H}_2\text{O}_2$  (Samanta, 2008) and the undesired hydrogenation of propylene to propane (Jenzer et al., 2001) have been reported as obstacles to the high PO selectivity and productivity. The limited PO yields are related to the low selectivity of  $\text{H}_2\text{O}_2$ , which is the rate limiting step for the direct synthesis of propylene oxide (Monnier, 2001). Furthermore, the palladium nanoparticles, responsible for  $\text{H}_2\text{O}_2$  formation, are also active in its hydrogenation and decomposition to water (Samanta, 2008) lowering its selectivity. Therefore, the controlled and separated feed of hydrogen in the system is a key parameter to control in order to improve the performance of the direct synthesis of propylene oxide by improving the  $\text{H}_2\text{O}_2$  and PO selectivity and safety concerns. This can be achieved with an engineering approach where the reactor design allows this optimization of the process. A possible reactor device to implement in the direct PO synthesis is the membrane reactor where controlled and separated feed of the reactants can easily be obtained.

In the present work we present a new catalytic membrane reactor concept for the direct propylene oxide synthesis in the liquid phase. This reactor design is the coupling of two consecutive reactions,  $\text{H}_2\text{O}_2$  synthesis and propylene epoxidation. The reactor design allows one to feed hydrogen and oxygen (in excess) through the membrane separately from the propylene. This configuration limits the hydrogenation of  $\text{H}_2\text{O}_2$  and propylene and improves the safety operation of the process. In this system, the PO production is optimized by maximizing separately the selectivity of  $\text{H}_2\text{O}_2$  (rate limiting step) and epoxidation. This optimization of the reactor concept consists in ensuring that  $\text{H}_2\text{O}_2$  synthesis step reaches selectivity targets of 50–60%, for hydrogen conversions higher than 10% (García-Serna et al., 2014) and PO selectivity of 50%, based on  $\text{H}_2\text{O}_2$ , and conversions of 90% (Cavani and Teles, 2009; Chowdhury et al., 2006). Moreover, the two reaction steps are then combined in a single reactor unit allowing the utilization of  $\text{H}_2\text{O}_2$  in situ produced immediately lowering its concentration in the reactor. This limits the decomposition of  $\text{H}_2\text{O}_2$  on the Pd catalyst improving even further the selectivity of  $\text{H}_2\text{O}_2$ , the rate limiting step of the overall process (Paunovic et al., 2015). The optimization of the reactor design was achieved with the implementation of a mathematical model which describes the two step reactor concept. Key parameters such as the membrane pore size, the membrane thicknesses and the gas concentrations are evaluated in order to ensure conversion and selectivity values which are competitive with existing processes (García-Serna et al., 2014; Cavani and Teles, 2009; Chowdhury et al., 2006). The optimized reactor design was then scaled up to a plant capacity of 300 kton/year of PO.

## 2. Reactor concept

A schematic representation of the catalytic membrane reactor is shown in Fig. 1. The reactor consists of two separated units where two consecutive reactions occur. The first reactor unit is a membrane contactor layer of Pd/SiO<sub>2</sub> catalyst where hydrogen and

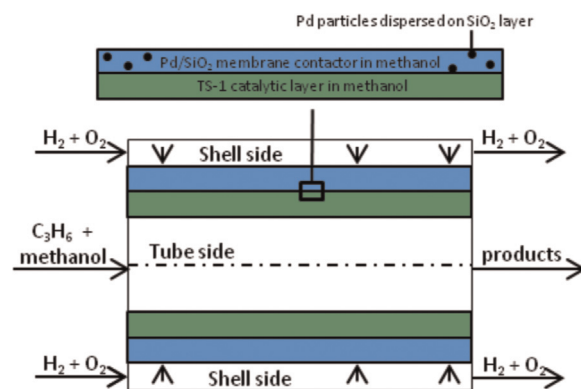


Fig. 1. Longitudinal section of a tubular membrane reactor and catalytic layers.

oxygen react to form  $\text{H}_2\text{O}_2$ . The concentrations of hydrogen and oxygen are kept outside the explosive limits. The second reactor unit is a titanium silicalite-1 (TS-1) catalytic layer. The  $\text{H}_2\text{O}_2$  produced in the first step reacts with propylene to PO on TS-1. The first requirement for both reaction steps to occur is the presence of a liquid phase (Cavani and Teles, 2009). The consensus in the literature is that methanol is the best solvent for the direct synthesis of PO due to high reaction rates (Russo et al., 2013) and high hydrogen solubility (Edwards et al., 2005). Furthermore, the presence of methanol improves the  $\text{H}_2\text{O}_2$  synthesis by removing the strongly adsorbed hydrogen peroxide from the catalytic sites. Methanol flow is also used to sweep the PO produced in the membrane reactor. Therefore, both catalytic layers are solvent filled. Oxygen and hydrogen, fed to the membrane contactor in the gas phase, dissolve and diffuse in the liquid filled pores of Pd/SiO<sub>2</sub> catalytic layer. These gases react on the Pd catalyst to form  $\text{H}_2\text{O}_2$ . The  $\text{H}_2\text{O}_2$  is either reduced to water in the presence of hydrogen (on Pd catalyst) or diffuses to the interface of the catalytic layers. Here,  $\text{H}_2\text{O}_2$  diffuses in the second layer (TS-1) and immediately reacts with propylene, present in the methanol, to form PO.

The optimization of the reactor design is achieved by determining key parameters such as the membrane pore size and thickness and the concentrations of the reactants. The membrane reactor concept, chosen for this study, presents a tubular geometry. Compared to the planar geometry, the tubular one is more advantageous for industrial applications due to the higher area provided and easier sealing of the edges. However, the present model applies also to planar membranes with similar operation conditions as the tubular one (reactants residence time and transport phenomena through the membrane contactor).

## 3. Model reactor approach

### 3.1. Modeling equations

The model consists of a set of mass balance equations which describes the concentrations profile of all the components through the reactor. A schematic representation of these profiles is shown in Fig. 2. The results from the simulation are used to calculate the conversion, the selectivity and the flux of the different compounds.

Two reactor units have been considered:

- Pd/SiO<sub>2</sub> catalytic membrane layer (unit 1),
- TS-1 layer catalytic layer (unit 2).

(a) *Unit 1*: A well mixed gas phase (hydrogen and oxygen) is considered to diffuse into the pores of the Pd/SiO<sub>2</sub> catalytic membrane layer filled with a stagnant liquid film (methanol). The

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