

# HYDROGEN PEROXIDE DIRECT SYNTHESIS: SELECTIVITY ENHANCEMENT BY A TRICKLE BED REACTOR

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## Summary

A Trickle Bed Reactor is used for the direct synthesis of hydrogen peroxide at high pressure. A catalyst based on Pd-CeS was used in a continuous, trickle-bed reactor. Manipulation of gas and liquid flow rates indicates that suitable combination of the contact time between the two phases can lead to dramatic selectivity variation, rising the value obtained in a discontinuous reactor up to 70%.

## Keywords

H<sub>2</sub>O<sub>2</sub>, TBR, Sustainability, Green CRE.

## Introduction

Hydrogen peroxide has always been considered a very interesting and environmentally friendly oxidant with applications confined mainly in unselective sectors such as the paper and textile industries and the treatment of waste waters.

The direct synthesis attracted renewed interest after 1980 due to the increased demand of H<sub>2</sub>O<sub>2</sub> as a green oxidant. It could soon compete with the indirect process if selectivity based on H<sub>2</sub> can be sufficiently high. The direct H<sub>2</sub> oxidation process has been extensively investigated, leading to a large number of publications in the last few years<sup>1,2</sup>. Recently, Basse and Jaeger<sup>3</sup> reported that a demonstration plant is ready to enter production. Research in the H<sub>2</sub>O<sub>2</sub> direct synthesis so far mostly focused on the identification and development of the catalyst. The present work is based on earlier work of Strukul and coworkers<sup>4</sup>, who synthesized several promising catalysts mono- and bimetallic catalysts. We are currently investigating opportunities of engineering the reaction, based on one of those good catalysts, rising the scale of investigation, implementing continuous operation. We illustrate how a trickle bed reactor allows to combine gas and liquid residence time to achieved enhancements of selectivity, up to 70%, for a catalyst based on Pd-CeS.

## Experimental

Catalytic tests were conducted in a trickle bed reactor (figure 1) at 10 bar and -10°C.

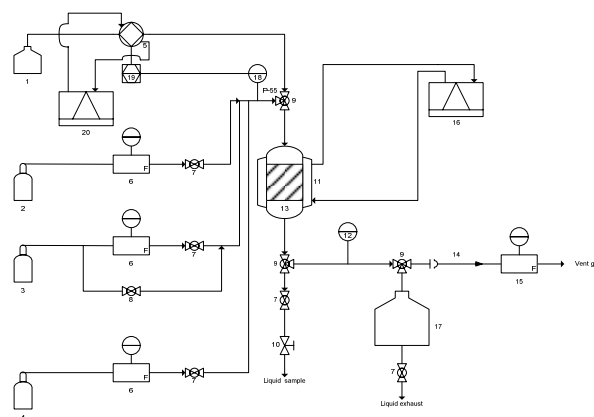


Figure 1: schematic of the experimental apparatus based on trickle bed reactor (TBR). 13 TBR, 17 tank collector

The overall length of the reactor is 300 mm and the internal diameter 11.5 mm. The gas reagents (O<sub>2</sub>/H<sub>2</sub>) were fed in the reactor with 2 mass flow controllers, as mixtures

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with CO<sub>2</sub>. Methanol was used as liquid solvent and then reaction medium and it was fed with a syringe pump. Sulfated ceria-supported catalysts, Pd-CeS<sup>4</sup> was the catalyst chosen for the reaction. It was diluted with silica (1:1 in weight), and the particles size of inert and catalyst was between 0.5 and 1 mm. The length of the catalyst bed was 7 mm. Three different liquid flow rates and seven different gas flow rates were investigated to perform the reaction in the trickle flow regime. Before every experiment the catalyst was reduced in situ with a flow of pure hydrogen for 1 h. After this procedure the bed is prewetted for several hours (4 h) to ensure complete internal saturation and external wetting and then the flow rate is increased until pulsing flow commences and afterwards the flow rate is reduces to the require level<sup>5</sup>.

## Results

Results are shown in Fig. 2 and Fig.3. Experiments carried out by feeding the methanol at 0.5 ml/min and the gas between 0.11 and 0.37 min/ml behave differently with respect to the case a larger liquid flow rate (2 ml/min) and the same gas flow. At a lower liquid flow rate, i.e. larger liquid residence time, the productivity (moles of H<sub>2</sub>O<sub>2</sub>/min) is larger, as expected.

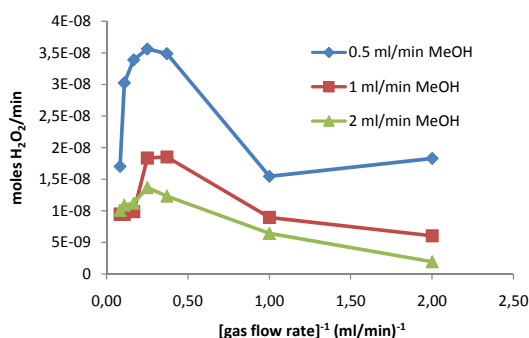


Figure 2: rate of H<sub>2</sub>O<sub>2</sub> production varying gas and liquid flow rates.

On the other hand, gas flow rate affects productivity non-linearly, passing through a maximum. Note that a larger H<sub>2</sub>O<sub>2</sub> flow rate at the lower liquid flow rate imply a gain in concentration. It also confirms the opportunities of affecting the reaction course in a TBR by suitably combining vapour-liquid equilibrium, interphase mass-transfer, and catalyst surface renewal.

The major concern in direct synthesis is poor selectivity because of the complex reaction network, involving product degradation steps and by-products (H<sub>2</sub>O). The assumption is that independent manipulation of gas and liquid contact time, as well as P and T, provides opportunities to control the reaction path through its mechanism. Fig. 3 shows how contact time between catalyst and liquid-gas components can affect the selectivity. The results achieved are two times higher than in the reactor used to develop and test the catalyst<sup>4</sup>, which was operated by continuously flowing gas through the liquid and solid, well stirred, batch suspension.

The continuous experiments in TBR were also reproduced with the same conditions and the agreement is quite good (<2% error). Further, the TBR operates under steady state conditions; after 12 h of continuous operation the H<sub>2</sub>O<sub>2</sub> productivity was preserved, not revealing deactivation.

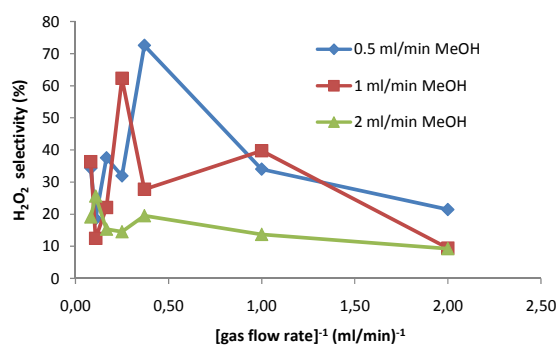


Figure 3: Selectivity of H<sub>2</sub>O<sub>2</sub> varying liquid and gas flow rates.

## Conclusions

Chemical engineering approach is needed to improve the direct synthesis of H<sub>2</sub>O<sub>2</sub> that goes through a mechanism involving active steps that affect selectivity. A continuous reactor such as a TBR can manipulate independently gas and liquid residence time on a fixed catalyst. We obtained a selectivity about two times higher than in a semibatch laboratory reactor with the same catalyst<sup>4</sup>. This fact suggest that development of H<sub>2</sub>O<sub>2</sub> direct synthesis requires i) further investigation on the reactor role, in addition to catalysts design ii) understanding on the limitation of batchwise testing novel catalysts. Gas and liquid flow rates can affect several aspects, mainly gas-liquid mass transfer rate and thus catalyst wetting and effective contact time between phases. Conditions for optimal operations have begun to shape, but the design space remains to be investigated systematically.

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