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Direct flow synthesis of H₂O₂ catalysed by palladium supported on sulfonated polystyrene resins

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1. Background and objectives

Hydrogen peroxide is a versatile and 'green' oxidising agent (the only by-product is water) widely used as a bleaching agent in the paper and textile industries.¹ It also finds many applications in the chemical industry, water treatment, semiconductor wafer cleaning and low-cost fuel cell technology.² However, it is routinely produced on the large scale by the environmentally unfriendly anthraquinone process. Therefore, direct H₂O₂ synthesis (from gaseous H₂ and O₂) has emerged as a desirable alternative.³ Flow chemistry and the microreactor technology have been successfully used for this process by several groups.⁴ Our interest lies in developing an integrated microfluidic process for H₂O₂ direct synthesis, possessing a minimized ecological footprint while improving the results described in the literature.

2. The catalysts

Catalytic systems based on palladium supported on strongly acidic macroreticular polystyrene resins have been described by several authors.⁵ We first used commercial Amberlyst-15[®] and loaded it with Pd^{II} following the method described by Blanco-Brieva *et al.* The experimental set-up is shown in case 3 and the results are presented in case 4.

As particle size of Amberlyst-15[®] is not convenient for microfluidic applications, we decided to prepare our own catalysts which possess a more narrow particle size distribution (40 - 80 µm).

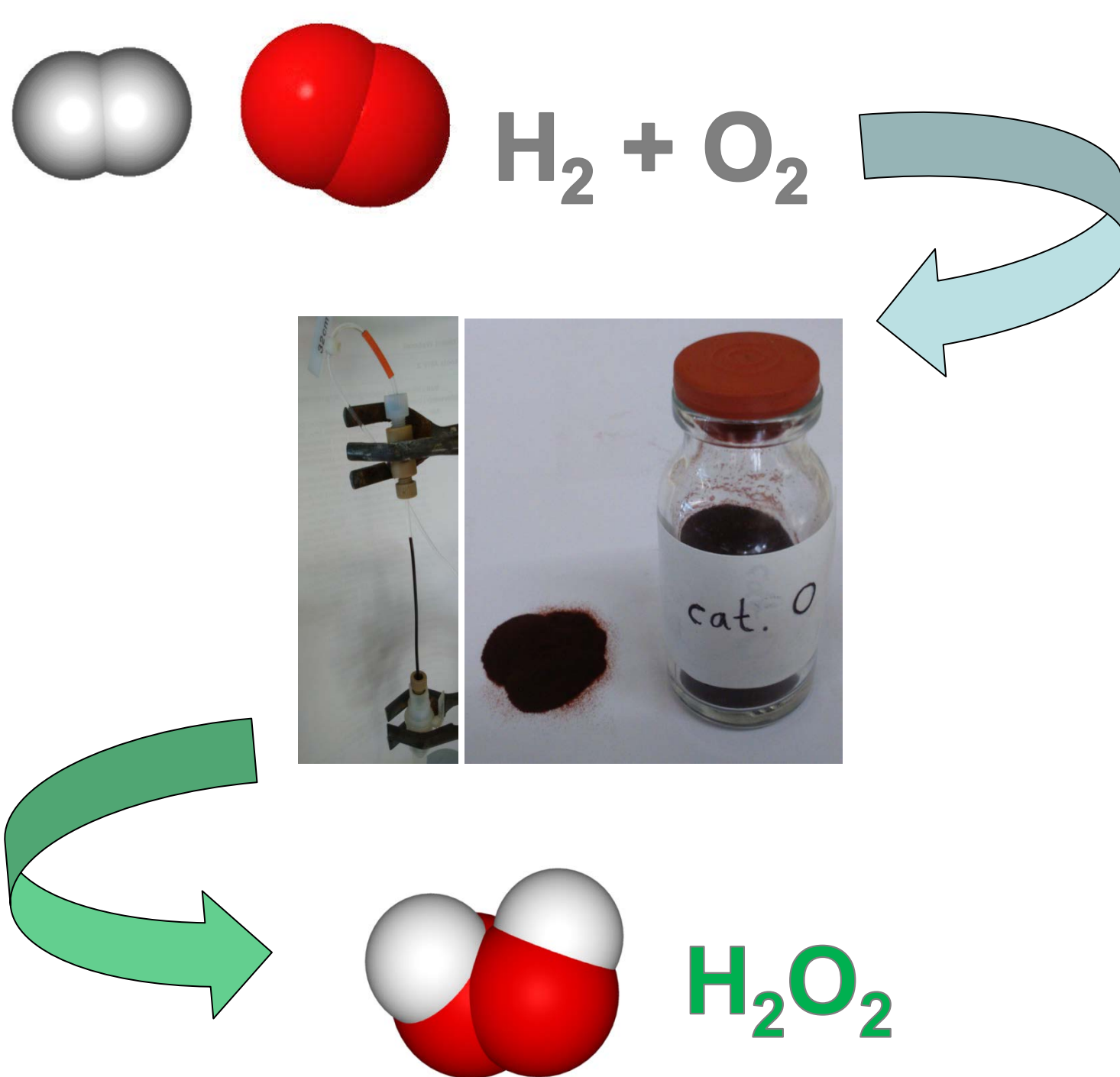
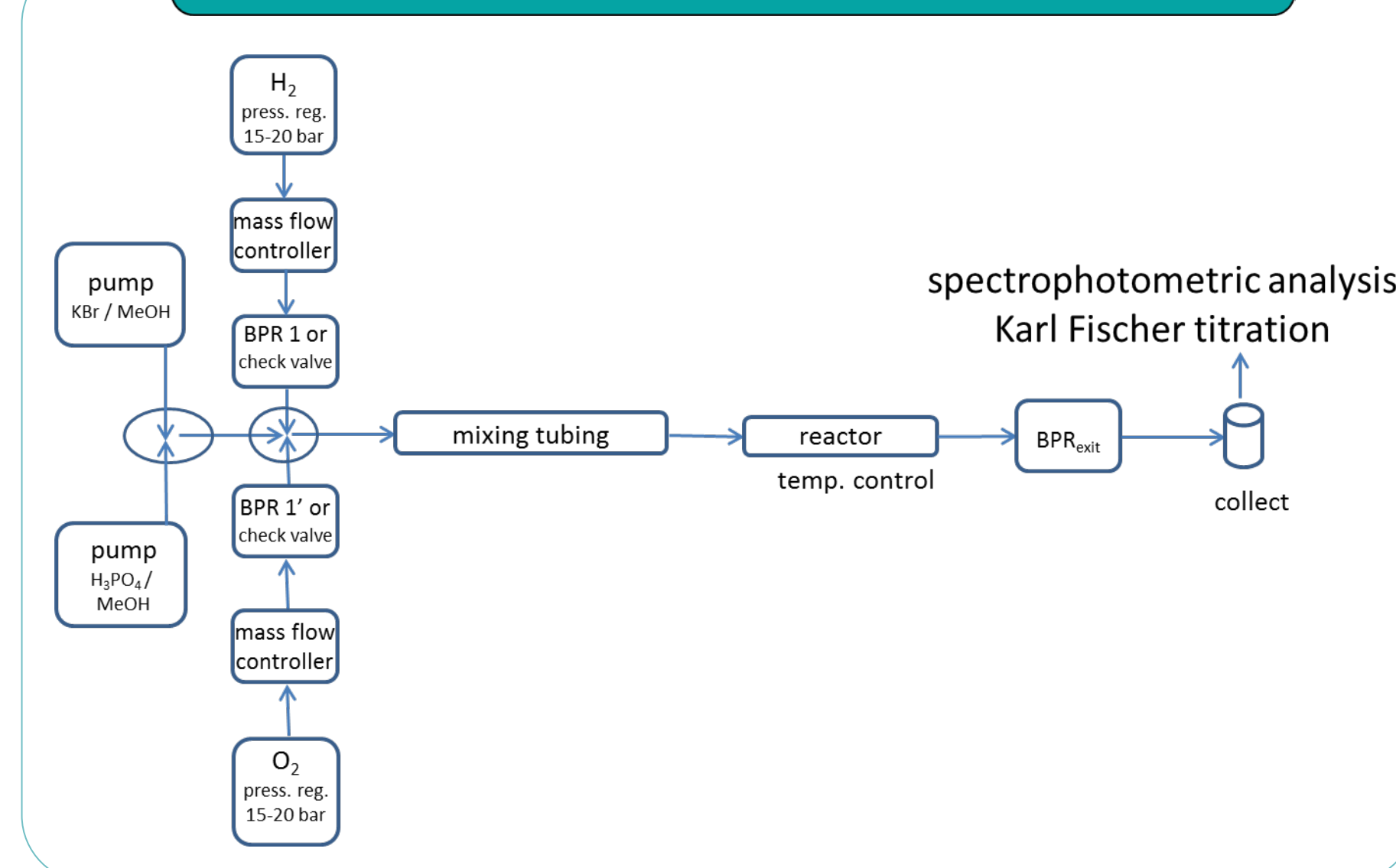
Preparation of catalysts:

- sulfonation : 4 g of resin, 10 mL ClSO₃H, 1,5 h, 0 to RT
- immobilization of palladium in a solvent



catalyst	Capacity (meq.g ⁻¹)	% Pd	Solvent for immo.
K	5,28	1	acetone/methanol
L	5,28	1	acetone
M	5,80	0,35	acetone
N	4,78	2	acetone
O	4,76	1	acetone

3. Experimental set up

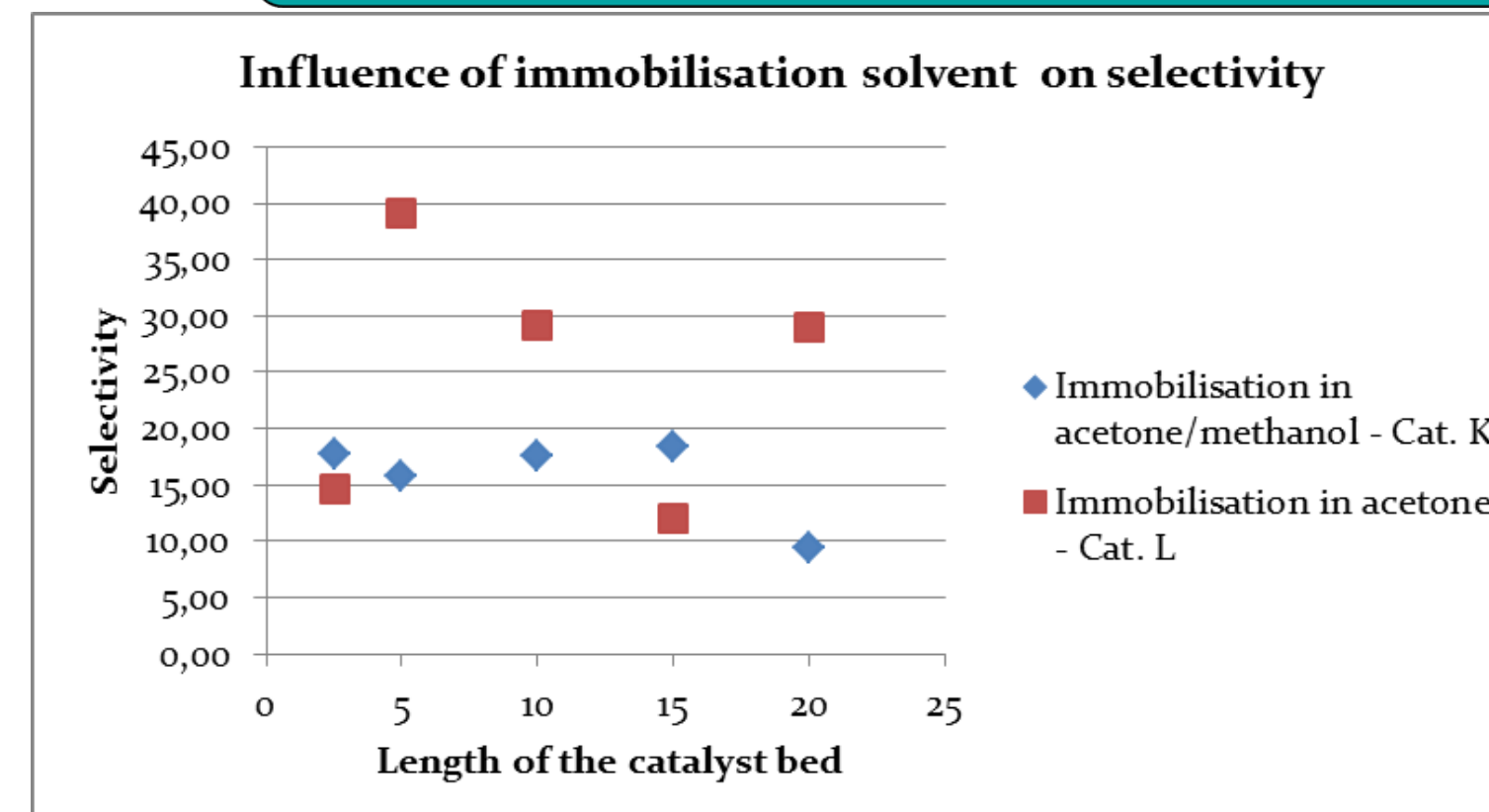


4. Results with Amberlyst-15[®]

solvent: MeOH, 10 ppm KBr, 0.01 M H₃PO₄; BPR_{exit} ... bar; system press. ... bar
flow (solv.) = 10 µL/min temp = 20°C length (cat) = ... cm
flow (H₂) = 1.67 sccm flow (O₂) = 3.33 sccm

exp.	length [cm]	[BPR _{exit} / bar]	average system press. [bar]	% wt. H ₂ O ₂
Dtube0053	2,5	8	11,0	2,00
Dtube0049	5	8	10,5	2,54
Dtube0052	10	8	10,2	2,69
Dtube0057	10	~17 (250 psi)	18,0	2,46
Dtube0056	15	8	8 - 10	2,15
Dtube0054	20	8	8 - 11	1,35

5. Influence of impregnation solvent



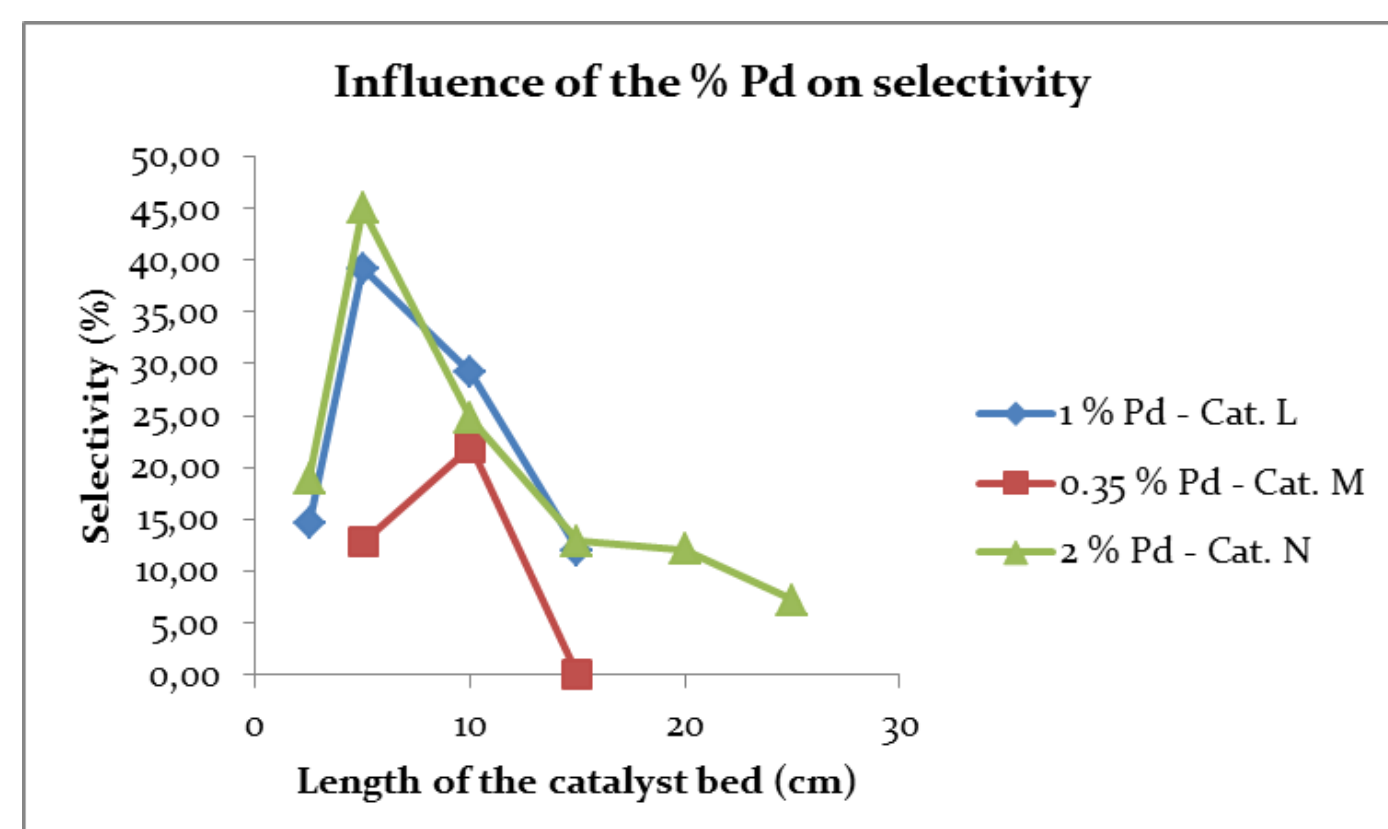
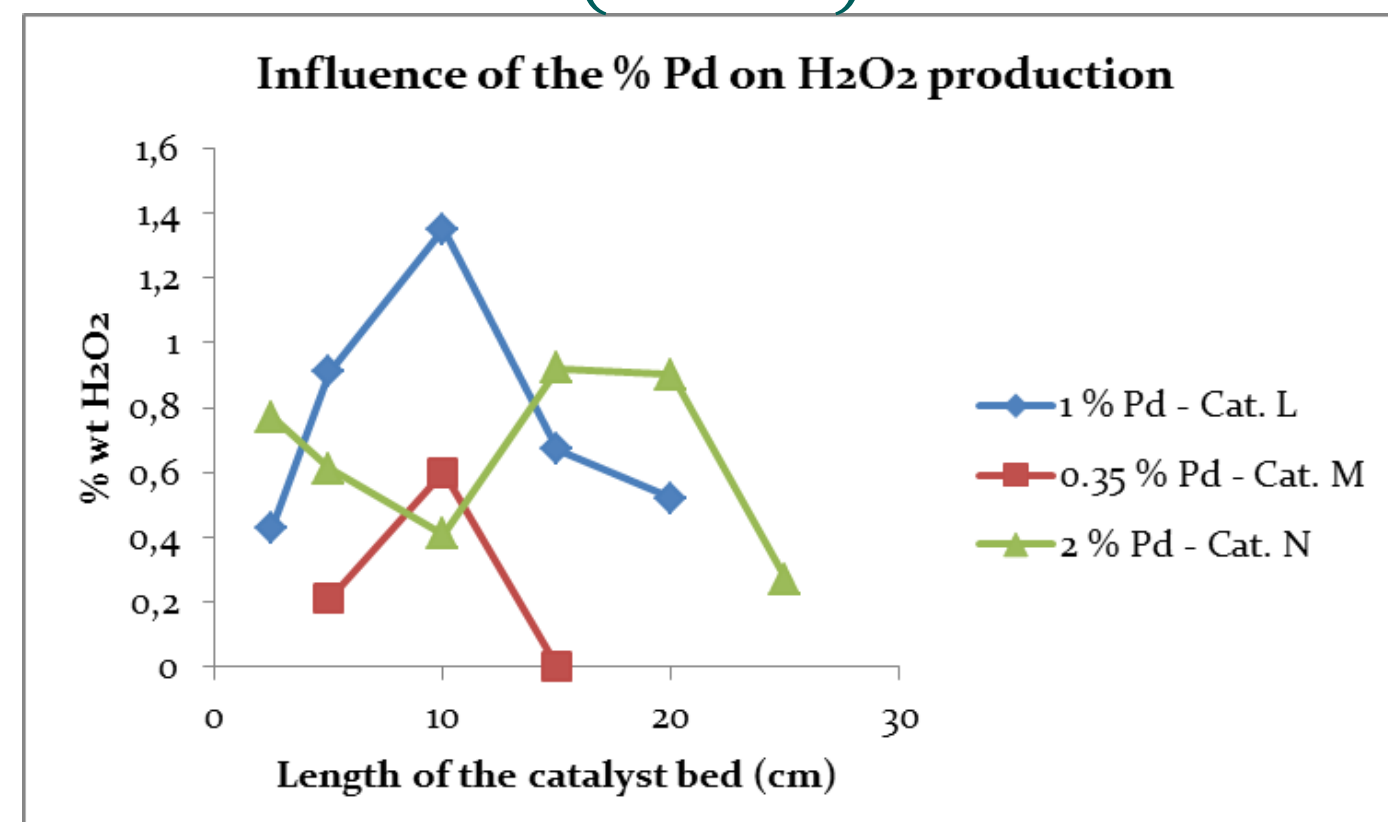
The selectivity S was defined as follows, owing to the existence of side reactions which led to the formation of water:

$$S = \frac{[H_2O_2]}{([H_2O_2] + [H_2O])}$$

These results revealed the importance of the solvent choice for impregnation. The differences are due to the catalytic species involved in the mechanism of the reaction, and more particularly to the oxidation state of palladium. Indeed, in the presence of methanol, Pd²⁺ is reduced into Pd⁰. We decided to only use acetone for the immobilisation.

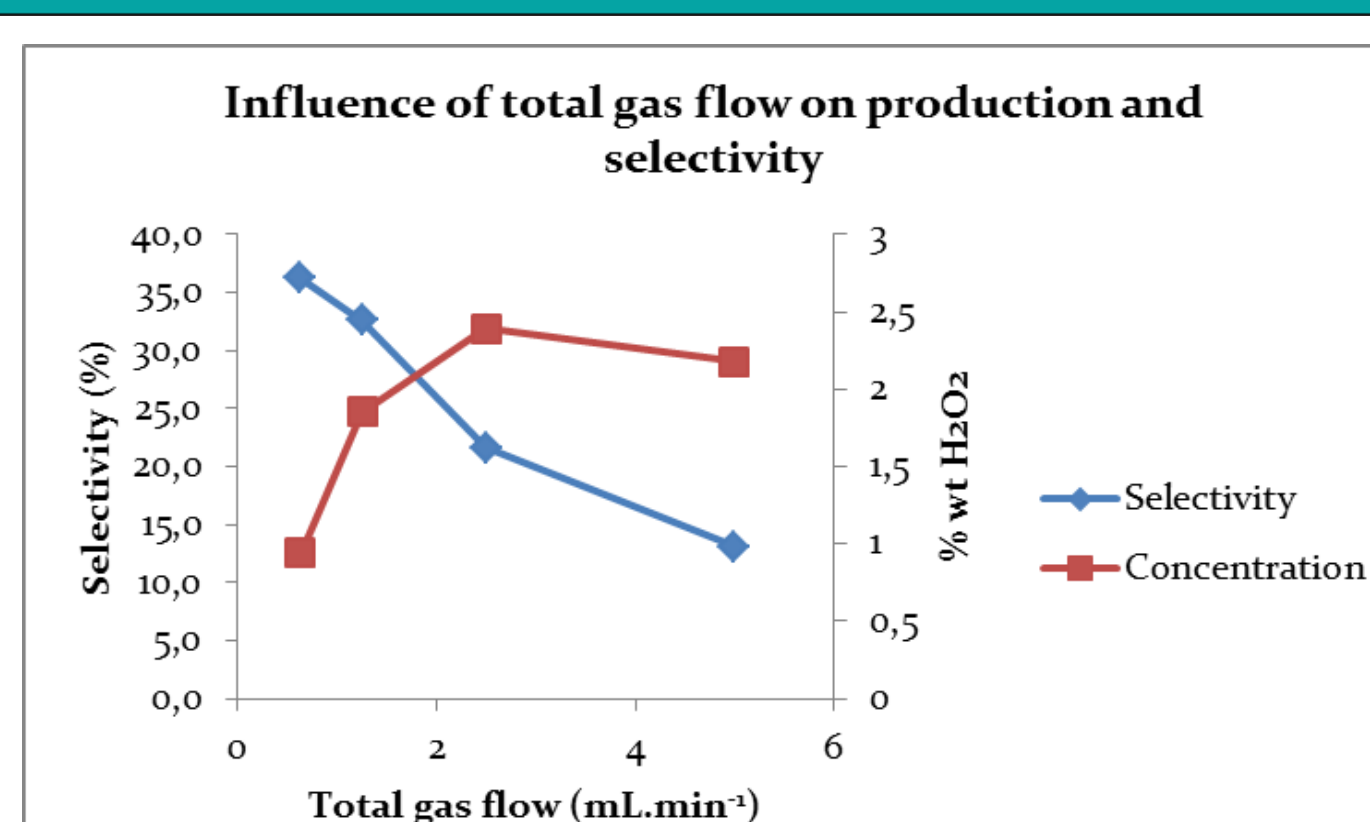
6. Influence of palladium percentage

$$wt = \frac{[H_2O_2]}{d(MeOH)}$$



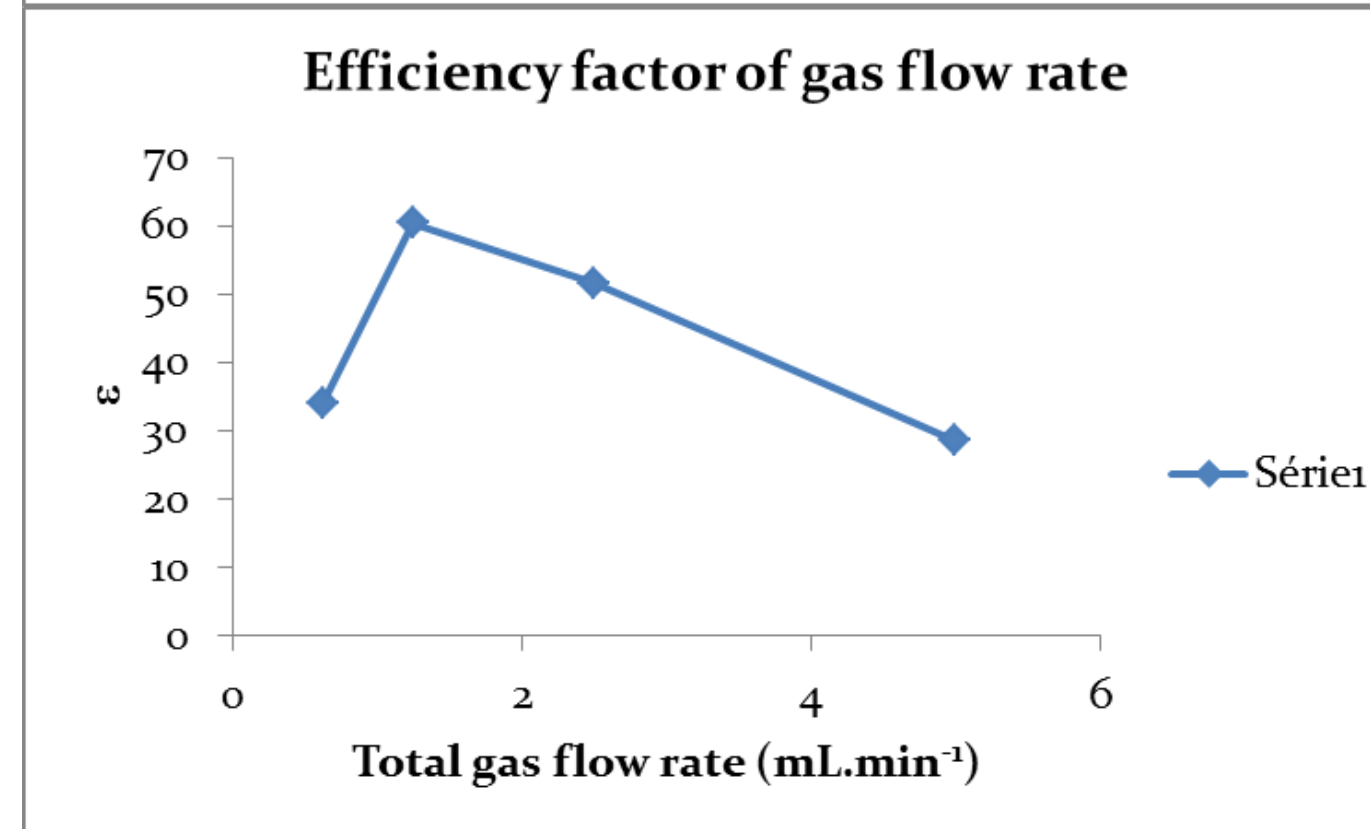
The variation of the amount of palladium on catalysts was next studied. In terms of production, catalysts with 1 % of immobilised Pd led to the best results. We obtained similar selectivities using the catalysts with 1% or 2% of palladium. We chose to keep 1 % of palladium for the next catalysts.

7. Influence of total gas flow



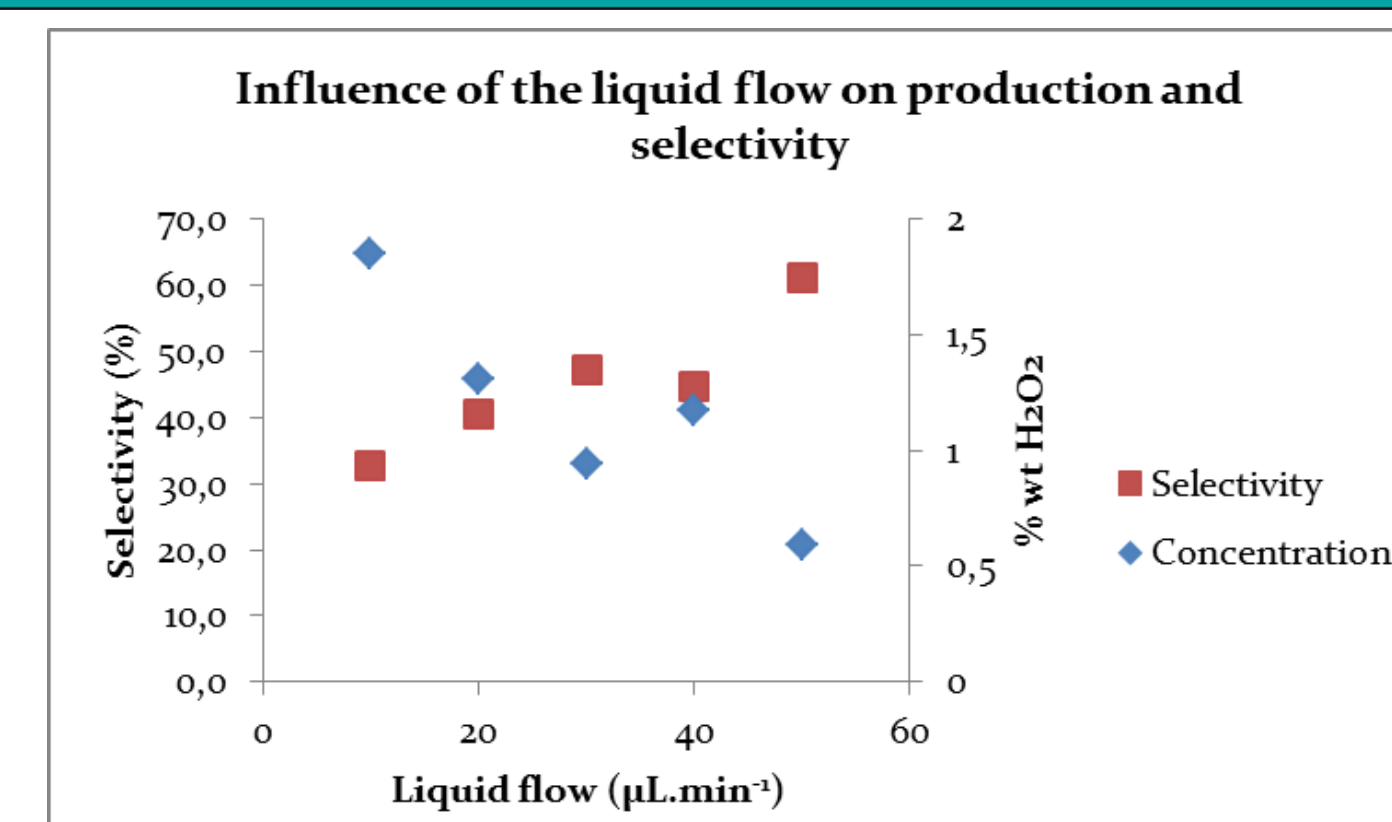
Catalyst O

$$\epsilon = wt * S$$



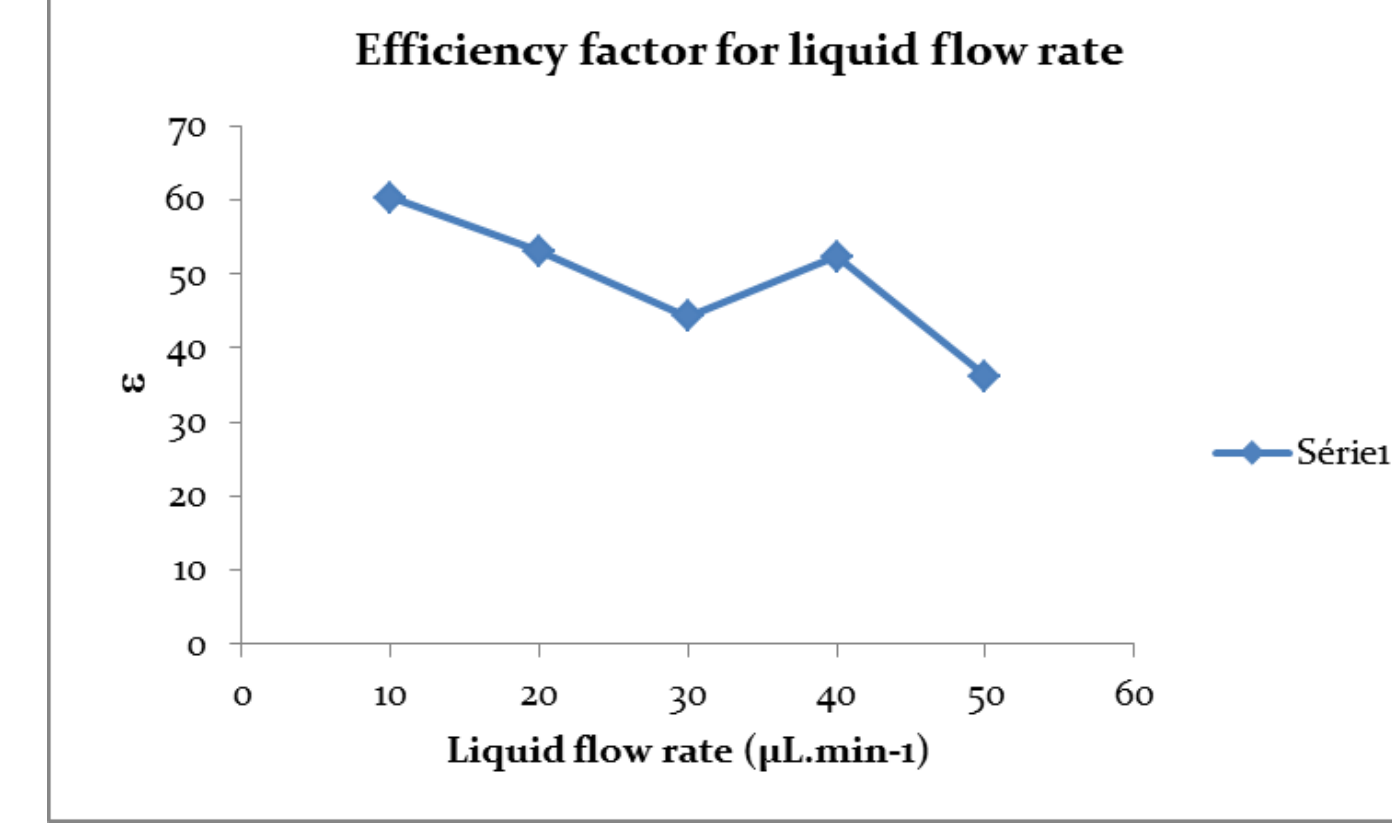
Increasing the total gas flow rate resulted in 2-fold improvement of H₂O₂ production. However, the selectivity is decreasing with high gas flow rate. By looking at the efficiency factor ε, we concluded that working with a total gas flow rate of 1.25 mL.min⁻¹ seemed to be the best compromise between H₂O₂ production and selectivity.

8. Influence of liquid flow



Catalyst O

$$\epsilon = wt * S$$



Increasing the total liquid flow rate (with a total gas flow of 1.25 mL.min⁻¹) enabled us to reach a selectivity of 60%, but H₂O₂ production remained low in these conditions. The efficiency factor ε suggests that we should work with higher liquid flow rate to obtain high selectivity. However to reach a satisfactory concentration (≥ 1% wt H₂O₂), we plan to work with moderate liquid flows.

9. Conclusion

We have been able to prepare resin-supported Pd catalysts on beads with small diameters and a narrow particle size distribution which are especially appropriate for microfluidic applications. The assays of direct H₂O₂ synthesis in flow gave promising results, in many cases superior than those described for similar systems in the literature. Up to 2-3 wt % and ~60% selectivity could be achieved. We identified that the impregnation of 1 % of palladium in acetone is the best choice for the preparation of the catalysts. The improvement of selectivity (at 1.25 sccm gas flow and 2*20 µL.min⁻¹ liquid flow) could be reached by studying the influence of a gradient of catalyst in the bed, by varying bromide concentration, and phosphoric acid. Further study of the composition of the surface of catalysts should allow us to identify the catalytically relevant species. Finally, optimizing the design of microreactors will be achieved through a kinetic study. Furthermore, we have learned to better master the reaction conditions, rendering the results more reproducible and easier to interpret.

References and Acknowledgments

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