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Direct synthesis of hydrogen peroxide in water in a continuous trickle bed reactor optimized to maximize productivity

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Hydrogen peroxide direct synthesis was studied in continuous mode over a 5% wt Pd/C commercial catalyst in a Trickle Bed Reactor. The target of the study was to maximize the hydrogen peroxide production. The catalyst was uniformly diluted in quartz sand at different concentrations to investigate their effects on the direct synthesis. The amount of catalyst and the distribution of the catalyst along the bed were optimized to obtain the highest possible yield. The distribution of the catalyst along the bed gave the possibility to significantly improve the selectivity and production of hydrogen peroxide (up to 0.5% under selected conditions). Higher production rate and selectivity were found when the catalyst concentration was decreased along the bed from the top to the bottom as compared to the uniformly dispersed catalyst. The H_2/Pd ratio was found to be an important parameter that has to be investigated in the hydrogen peroxide direct synthesis. The effect of a pretreatment of the catalyst with a solution of sodium bromide and phosphoric acid was studied; the results showed how a catalyst pretreatment can lead to a real green hydrogen peroxide synthesis in water. Some optimization guidelines are also provided.

1. Introduction

Green chemistry and Green Engineering are becoming year after year an important philosophy-in-practice in Chemical Engineering research both in Academia and Industry. Hydrogen peroxide and hydrogen peroxide direct synthesis are part of this philosophy. Hydrogen peroxide is an effective green chemical, it is the simplest of the peroxides, the byproducts are only oxygen and water and its oxidation potential is high. In a future vision of a sustainable world, hydrogen peroxide will replace all those chemicals with high oxidation potential that need a complicated and expensive waste treatment after their use in chemical synthesis.[1–3] The current process to produce hydrogen peroxide cannot be considered green in terms of the organics used (*i.e.* anthraquinone); for that reason the direct synthesis is becoming an interesting possibility to produce hydrogen peroxide for *in situ* applications.[1–3] There are other options, such as the electrochemical reduction of oxygen *via* a four-step-one-electron reaction into a superoxide, hydrogen peroxide and finally a hydroxyl radical.[4–6]

The last process is excellent in terms of atom economy, not needing hydrogen, and it is probably one of the best options, because this is what nature does. In this paper we study the direct synthesis as an intermediate option between using anthraquinone (traditional) and producing H_2O_2 without the need of hydrogen (biomimicry and electrochemical reduction of oxygen to superoxide).

The market that will be of particular interest for the direct synthesis includes oxidation processes like the propylene oxide formation, pulp bleaching, electronics and wastewater treatment as examples.[3] The epoxidation of propylene into propylene oxide is one of the most important petrochemical applications for H_2O_2 produced *via* direct synthesis.[7] A concentrated H_2O_2 is necessary, because of the side reactions of H_2O forming glycols with the propylene oxide. The use of H_2O as a solvent instead of methanol for the PO process reduces the side products considerably over the use of methanol (that forms methoxy propanols). On the other hand, methanol is convenient as it dissolves both propylene and propylene oxide, while water creates a two-phase liquid–liquid reaction.

Either for the traditional anthraquinone synthesis or the direct synthesis, the concentrations of H_2O_2 are normally low (*i.e.* below 1% wt typically) and the need of a downstream concentration is there in both cases. Producing H_2O_2 at high concentrations directly has the drawback of a reduced selectivity, as the active metal (*e.g.* palladium) causes both hydrogenation and decomposition. For decomposition a high H_2O_2 concentration is extremely inconvenient, as decomposition is a first order reaction with H_2O_2. Furthermore, the percentage of decomposition during the concentration operations, *i.e. via*

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vacuum distillation, is considerably lower than by reaction. That is why in the traditional process, 30%, 50% and 70% H_2O_2 solutions are produced *via* distillation. The direct synthesis avoids transportation costs of concentrated hydrogen peroxide and wastewater treatment. So far, the auto-oxidation process is still the most popular process to produce hydrogen peroxide and the continuous direct synthesis process is not sufficiently developed.[2]

In the last two decades, industry[8–11] and academia[12–27] tried hard to make progress in the direct synthesis research focusing on catalyst design, reactor systems and modeling. The results obtained are promising and the combination of different kinds of expertise will lead to novel solutions and to a big step further in the field.

Catalyst design and improvement of them in the direct synthesis covers around 80% of the publications. Usually noble metals were chosen as the active phase, and monometallic[12,17,28,29] and bimetallic[18,22,30,31] catalysts based on palladium were employed. The supports for the active phase cover different inorganic and organic materials. Modifications to the supports were also investigated. Recently the attention paid to different kinds of continuous reactors became strong. Microreactors,[20,21,32] continuous membrane reactors,[26] upflow reactors and trickle bed reactors (TBRs)[13–15,33] showed the possibility to continuously produce hydrogen peroxide in a promising efficient way. The issues that are still unsolved in the direct synthesis are selectivity, concentration and catalyst deactivation. The selectivity and concentration of hydrogen peroxide are intimately related, as it is difficult to obtain high concentrations of hydrogen peroxide together with high selectivity.[14] When halides and acids are used as promoters, selectivity increases considerably but leaching of the active metal may occur. In the same way, at high concentrations of H_2O_2, the selectivity is usually low and *vice versa*, as indicated before. This fact is due to the nature of the catalyst; the active metal/metals active for the direct synthesis are also active for the direct formation of water, hydrogenation and decomposition of hydrogen peroxide.[29,34] The direct formation of water is difficult to measure; hydrogenation was well demonstrated as a key reaction during the direct synthesis and the decomposition gives a small contribution to the overall reaction rate as described previously.[29,34] The numerous investigations on direct synthesis try to understand the phenomena that regulate the hydrogenation reaction aiming to switch it off.[18]

Here we investigate the direct synthesis in a down-flow trickle bed reactor, using water as a reaction medium. The catalyst (due to its low amount) was dispersed in quartz sand. The aim of the work is to set variables in order to maximize the reaction over a commercial catalyst. The first part of the work deals with the conventional way to optimize the productivity, finding the suitable temperature, pressure and gas and liquid flow rates. The second part is focused on unconventional ways to optimize the reactor parameters, such as transient experiments (changing the liquid feed during the experiments) and changing the concentration of the catalyst along the catalytic bed. The third part takes into consideration the possibility of enhancing the concentration of the hydrogen peroxide by a subsequent distillation column.

In this work we demonstrate that: (1) the H_2/Pd ratio plays an important role during the direct synthesis[15,29]; (2) the control of reactor and reactor conditions shifts the balance in favour of productivity.

2. Results and discussion

A set of 75 experiments was designed in order to study the effect of the pressure, liquid and gas flow rates, temperature, amount of catalyst and volume of bed. The trickle bed reactor operated in continuous mode modifying the experimental conditions. The bed was charged with the quartz sand plus catalyst mixture and operated under different conditions. The stabilization time ranged between 30 and 90 min depending on the flow rate and the magnitude of the step. After the system stabilizes, three measurements were taken and the average was calculated. Table 1 contains the experimental conditions and the average results.

The effects of the main variables have been divided according to the physical–chemical influence on the reaction outcomes: primarily, mass transfer, kinetics and catalysis.

2.1. Mass transfer related influences

The reactions take place at the catalyst surface. The gas reagents, *i.e.* H_2 and O_2, must dissolve from a gas phase into a liquid phase and then be transported to the catalyst.

Oxygen is in excess over the stoichiometric need *versus* hydrogen; therefore, the limiting reagent due to mass transfer limitations is hydrogen.

2.1.1. Influence of H_2 partial pressure. The variation of the H_2 partial pressure changes the equilibrium solubility of H_2 in the liquid phase, which modifies the mass transfer differential concentration and ultimately the concentration of H_2 available at the surface of the catalyst.

The solubility of H_2 in water between 5 and 35 °C and at hydrogen partial pressures between 0.27 and 1.45 bara were simulated using Aspen Plus ONE7.1 using the PRSK thermodynamic package[35] as shown in Table 1.

2.1.1.1. Influence of H_2 inlet concentration. Due to safety reasons, it is necessary to operate away from the flammability region, and this implies using inlet H_2 concentrations lower than 4.6 mol%. As an additional safety measure, in the set-up, we operated with the H_2 premixed with CO_2 in the cylinder. To increase the mass transfer, the maximum H_2 in the cylinder was 5 mol% (4 mol% in the final reaction mixture, under the flammability restriction). Then, the experimental system was limited by the maximum reaction pressure up to 28 barg (because that of the gas cylinder mixture 5% H_2/CO_2 is up to a maximum of 32 barg).

To reveal the effect of the inlet concentration, we carried out two experiments (runs #01 and #02) using 2.5 mol%-H_2/97.5 mol%-CO_2 and 5 mol%-H_2/95 mol%-CO_2 cylinders, respectively.

Table 1 Design of the experiment table for the study of H_2O_2 direct synthesis in a trickle bed reactor. Reactant medium: H_2O_2 + 0.004 M NaBr + 0.003 M H_3PO_4

Run	Total press. (barg)	Temp. (°C)	LFR (mL min^{-1})	GFR (mL min^{-1})	H_2 inlet conc. (% mol)	H_2 inlet flow (mmol min^{-1})	H_2 inlet press. (bara)	H_2 solubility (mol mol^{-1})	Cat. (% Pd/C)	Catalyst amount (mg cat)	Bed volume (mL)	Productiv. (mmol min^{-1})	Yield (%)	H_2O_2 conc. (% wt/vol)
#01	10	25	1.00	4.00	2.5%	37.5	0.27	2.80E-06	5%	150	80	11.6	30.9%	0.039%
#02	10	25	1.00	4.00	5%	75.0	0.55	2.80E-06	5%	150	80	27.8	37.1%	0.095%
#03	10	25	1.00	2.00	5%	37.5	0.55	2.80E-06	5%	150	80	7.5	19.9%	0.025%
#04	28	25	0.25	4.00	5%	235.6	1.45	1.00E-05	5%	150	80	64.4	27.3%	0.875%
#05	28	25	0.50	4.00	5%	235.6	1.45	1.00E-05	5%	150	80	75.5	32.0%	0.513%
#06	28	25	1.00	4.00	5%	235.6	1.45	1.00E-05	5%	150	80	80.1	34.0%	0.272%
#07	28	25	1.50	4.00	5%	235.6	1.45	1.00E-05	5%	150	80	85.0	36.1%	0.193%
#08	28	25	2.00	4.00	5%	235.6	1.45	1.00E-05	5%	150	80	89.4	38.0%	0.152%
#09	28	25	0.25	4.00	5%	235.6	1.45	1.00E-05	5%	75	40	88.6	37.6%	1.205%
#10	28	25	0.50	4.00	5%	235.6	1.45	1.00E-05	5%	75	40	114.7	48.7%	0.780%
#11	28	25	1.00	4.00	5%	235.6	1.45	1.00E-05	5%	75	40	125.4	53.2%	0.426%
#12	28	25	1.50	4.00	5%	235.6	1.45	1.00E-05	5%	75	40	146.2	62.1%	0.331%
#13	28	25	2.00	4.00	5%	235.6	1.45	1.00E-05	5%	75	40	149.4	63.4%	0.254%
#14	28	5	1.00	4.00	5%	235.6	1.45	9.94E-06	5%	75	40	62.1	26.3%	0.211%
#15	28	10	1.00	4.00	5%	235.6	1.45	9.83E-06	5%	75	40	66.9	28.4%	0.227%
#16	28	15	1.00	4.00	5%	235.6	1.45	9.82E-06	5%	75	40	71.2	30.2%	0.242%
#17	28	20	1.00	4.00	5%	235.6	1.45	9.90E-06	5%	75	40	110.5	46.9%	0.376%
#18	28	35	1.00	4.00	5%	235.6	1.45	1.05E-05	5%	75	40	114.1	48.4%	0.388%
#19	28	40	1.00	4.00	5%	235.6	1.45	1.09E-05	5%	75	40	123.9	52.6%	0.421%
#20	15	5	1.00	4.00	5%	105.0	0.80	4.19E-06	5%	30	80	28.3	26.9%	0.096%
#21	15	10	1.00	4.00	5%	105.0	0.80	4.25E-06	5%	30	80	32.6	31.0%	0.111%
#22	15	15	1.00	4.00	5%	105.0	0.80	4.34E-06	5%	30	80	20.8	19.8%	0.071%
#23	15	5	1.00	4.00	5%	105.0	0.80	4.19E-06	5%	150	80	64.7	61.6%	0.220%
#24	15	15	1.00	4.00	5%	105.0	0.80	4.34E-06	5%	150	80	67.3	64.1%	0.229%
#25	15	25	1.00	4.00	5%	105.0	0.80	4.62E-06	5%	150	80	67.3	64.1%	0.229%
#26	15	35	1.00	4.00	5%	105.0	0.80	5.01E-06	5%	150	80	64.1	61.0%	0.218%
#27	5	5	1.00	4.00	5%	34.0	0.30	1.17E-06	5%	150	80	17.2	50.7%	0.059%
#28	5	15	1.00	4.00	5%	34.0	0.30	1.29E-06	5%	150	80	20.0	58.8%	0.068%
#29	5	25	1.00	4.00	5%	34.0	0.30	1.45E-06	5%	150	80	21.2	62.3%	0.072%
#30	5	35	1.00	4.00	5%	34.0	0.30	1.63E-06	5%	150	80	21.7	63.8%	0.074%
#31	15	5	1.00	4.00	5%	105.0	0.80	4.19E-06	5%	100	80	63.3	60.3%	0.215%
#32	15	15	1.00	4.00	5%	105.0	0.80	4.34E-06	5%	100	80	66.6	63.4%	0.226%
#33	15	25	1.00	4.00	5%	105.0	0.80	4.62E-06	5%	100	80	66.4	63.2%	0.226%
#34	15	35	1.00	4.00	5%	105.0	0.80	5.01E-06	5%	100	80	63.0	60.0%	0.214%
#35	5	5	1.00	4.00	5%	34.0	0.30	1.17E-06	5%	100	80	18.2	53.5%	0.062%
#36	5	15	1.00	4.00	5%	34.0	0.30	1.29E-06	5%	100	80	20.9	61.4%	0.071%
#37	5	25	1.00	4.00	5%	34.0	0.30	1.45E-06	5%	100	80	22.1	65.0%	0.075%
#38	5	35	1.00	4.00	5%	34.0	0.30	1.63E-06	5%	100	80	22.0	64.7%	0.075%
#39	15	5	1.00	4.00	5%	105.0	0.80	4.19E-06	5%	75	80	58.5	55.7%	0.199%
#40	15	15	1.00	4.00	5%	105.0	0.80	4.34E-06	5%	75	80	64.2	61.1%	0.218%
#41	15	25	1.00	4.00	5%	105.0	0.80	4.62E-06	5%	75	80	67.3	64.1%	0.229%
#42	15	35	1.00	4.00	5%	105.0	0.80	5.01E-06	5%	75	80	67.8	64.5%	0.230%
#43	5	5	1.00	4.00	5%	34.0	0.30	1.17E-06	5%	75	80	20.6	60.7%	0.070%
#44	5	15	1.00	4.00	5%	34.0	0.30	1.29E-06	5%	75	80	20.1	59.1%	0.068%
#45	5	25	1.00	4.00	5%	34.0	0.30	1.45E-06	5%	75	80	21.8	64.1%	0.074%

Table 1 *(Contd.)*

Run	Total press. (barg)	Temp. (°C)	LFR (mL min^{-1})	GFR (mL min^{-1})	H_2 inlet conc. (% mol)	H_2 inlet flow (mmol min^{-1})	H_2 inlet press. (bara)	H_2 solubility (mol mol^{-1})	Cat. (% Pd/C)	Catalyst amount (mg cat)	Bed volume (mL)	Productiv. (mmol min^{-1})	Yield (%)	H_2O_2 conc. (% wt/vol)
#46	5	35	1.00	4.00	5%	34.0	0.30	1.63E-06	5%	75	80	23.4	68.9%	0.080%
#47	15	5	1.00	4.00	5%	105.0	0.80	4.19E-06	5%	75	40	72.3	68.9%	0.246%
#48	15	15	1.00	4.00	5%	105.0	0.80	4.34E-06	5%	75	40	77.8	74.1%	0.265%
#49	15	25	1.00	4.00	5%	105.0	0.80	4.62E-06	5%	75	40	55.6	53.0%	0.189%
#50	15	35	1.00	4.00	5%	105.0	0.80	5.01E-06	5%	75	40	60.5	57.7%	0.206%
#51	28	10	1.00	4.00	5%	235.6	1.45	9.83E-06	5%	150	80	73.7	31.3%	0.251%
#52	28	15	1.00	4.00	5%	235.6	1.45	9.82E-06	5%	150	80	76.6	32.5%	0.260%
#53	28	20	1.00	4.00	5%	235.6	1.45	9.90E-06	5%	150	80	78.9	33.5%	0.268%
#54	28	25	1.00	4.00	5%	235.6	1.45	1.00E-05	5%	150	80	80.0	34.0%	0.272%
#55	28	30	1.00	4.00	5%	235.6	1.45	1.03E-05	5%	150	80	79.2	33.6%	0.269%
#56	28	35	1.00	4.00	5%	235.6	1.45	1.05E-05	5%	150	80	78.8	33.5%	0.268%
#57	28	5	1.00	4.00	5%	235.6	1.45	9.94E-06	5%	100	80	83.3	35.4%	0.283%
#58	28	15	1.00	4.00	5%	235.6	1.45	9.82E-06	5%	100	80	92.0	39.0%	0.313%
#59	28	25	1.00	4.00	5%	235.6	1.45	1.00E-05	5%	100	80	91.9	39.0%	0.312%
#60	28	35	1.00	4.00	5%	235.6	1.45	1.05E-05	5%	100	80	82.7	35.1%	0.281%
#61	28	5	1.00	4.00	5%	235.6	1.45	9.94E-06	5%	75	80	127.9	54.3%	0.435%
#62	28	15	1.00	4.00	5%	235.6	1.45	9.82E-06	5%	75	80	116.4	49.4%	0.396%
#63	28	25	1.00	4.00	5%	235.6	1.45	1.00E-05	5%	75	80	112.6	47.8%	0.385%
#64	28	35	1.00	4.00	5%	235.6	1.45	1.05E-05	5%	75	80	98.7	41.9%	0.336%
#65	28	5	1.00	4.00	5%	235.6	1.45	9.94E-06	5%	300	80	124.3	52.7%	0.423%
#66	28	15	1.00	4.00	5%	235.6	1.45	9.82E-06	5%	300	80	97.5	41.4%	0.332%
#67	28	25	1.00	4.00	5%	235.6	1.45	1.00E-05	5%	300	80	76.7	32.5%	0.261%
#68	28	35	1.00	4.00	5%	235.6	1.45	1.05E-05	5%	300	80	61.9	26.3%	0.226%
#69	28	5	1.00	4.00	5%	235.6	1.45	9.94E-06	5%	50/25	40/40	132.9	56.4%	0.452%
#70	28	15	1.00	4.00	5%	235.6	1.45	9.82E-06	5%	50/25	40/40	135.3	57.4%	0.460%
#71	28	25	1.00	4.00	5%	235.6	1.45	1.00E-05	5%	50/25	40/40	122.4	51.9%	0.416%
#72	28	35	1.00	4.00	5%	235.6	1.45	1.05E-05	5%	50/25	40/40	115.3	48.9%	0.392%
#73	28	5	1.00	4.00	5%	235.6	1.45	9.94E-06	5%	37.5/25/12.5	26.6/26.6/26.6	147.5	62.6%	0.502%
#74	28	15	1.00	4.00	5%	235.6	1.45	9.82E-06	5%	37.5/25/12.5	26.6/26.6/26.6	141.4	60.0%	0.481%
#75	28	25	1.00	4.00	5%	235.6	1.45	1.00E-05	5%	37.5/25/12.5	26.6/26.6/26.6	126.7	53.8%	0.431%
#76	28	35	1.00	4.00	5%	235.6	1.45	1.05E-05	5%	37.5/25/12.5	26.6/26.6/26.6	117.2	49.7%	0.398%

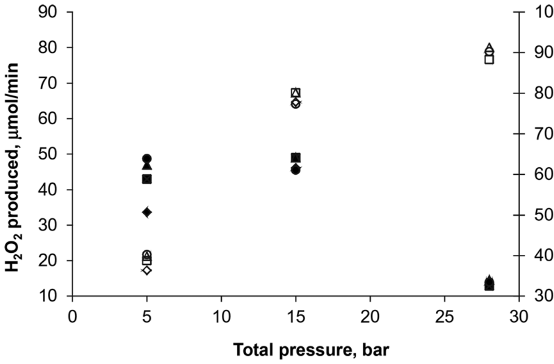

Fig. 1 H_2O_2 production *vs.* total pressure for 150 mg 5% Pd/C and 80 mL SiO_2 bed and 4% mol-H_2. H_2O_2 production (µmol min^{-1}): (◊) 5 °C, (□) 15 °C and (△) 25 °C. H_2O_2 Yield (%): (◆) 5 °C, (■) 15 °C, (▲) 25 °C and (●) 35 °C.

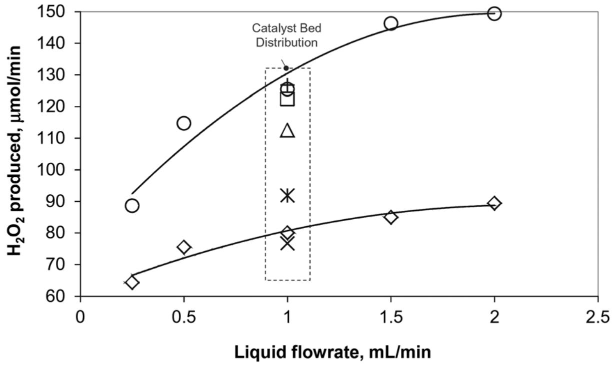

Fig. 2 H_2O_2 production *vs.* liquid flow rate for a 5% Pd/C and SiO_2 bed at 28 barg and 25 °C. H_2O_2 production for different catalyst distributions in the trickle bed reactor: (x) 300 mg of Pd/C in 80 mL bed, (◊) 150 mg of Pd/C in 80 mL bed, (*) 100 mg of Pd/C in 80 mL bed, (△) 75 mg of Pd/C in 80 mL bed, (○) 75 mg of Pd/C in 40 mL bed, (□) 50/25 mg of Pd/C in 40/40 mL bed and (+) 37.5/25/12.5 mg of Pd/C in 26.6/26.6/26.6 mL bed.

The productivity increased considerably (more than double) when the H_2 was doubled, producing 27.8 µmol-H_2O_2 min^{-1} *vs.* 11.6 µmol-H_2O_2 min^{-1} with 2 mol%-H_2, as more H_2 is dissolved and available for the H_2O_2 direct synthesis. However, the efficiency of the process decreased, as can be seen by comparing the yields. The yield using 4 mol%-H_2 (0.55 bara of H_2) was 37.1% compared to 30.9% at 2 mol%-H_2 (0.27 bara of H_2). This means that more H_2O_2 is hydrogenated and that H_2O production by direct synthesis is enhanced proportionally.

2.1.1.2. Influence of total reaction pressure. The system was investigated at three different total pressures using 150 mg of 5% Pd/C catalyst, ensuring that the system was mass transfer controlled (runs #06, #23–#30 and #51–#56). Fig. 1 shows that increasing pressure increased the quantity of H_2O_2 formed. As can be seen, the effect of temperature was almost negligible compared to the pressure effect. This means that the increase in kinetics does not increase the production, because of mass transfer limitations. The increase in the total pressure implies an increase in the hydrogen flow rate at the reactor entrance, as we have decided to maintain the same gas hydrodynamics of 4 mL min^{-1} of gas inside the TBR in this work. The yield in this case has to be analysed. The yield of the reaction is constant at 50% changing from 5 barg to 15 barg, but it decreases down to 35% at 28 barg. The effect shows how between 5 and 15 barg the system is almost controlled by the mass transfer of hydrogen, while at 28 barg all the hydrogen is not consumed, or at least it is not consumed for producing H_2O_2. Again, as in the previous section, the excess of H_2 dissolves and is available for the undesirable hydrogenation at the end of the reactor (where the concentration of H_2O_2 is higher), as will be shown later in section 2.1.2. Therefore, the increase in the total pressure is an option to increase the mass transfer, but care must be taken to control the kinetics, especially when higher concentrations of H_2O_2 are available.

2.1.1.3. Influence of the O_2/H_2 ratio. Several authors stated that the O_2/H_2 ratio must be high to ensure minimization of H_2O_2 decomposition and an oxidizing atmosphere. However, we carried out two experiments to show this fact (runs #01 and #37); an excess of O_2 is not as profitable as expected, probably because of the inhibition of certain sites on the catalyst. As can be seen, a ratio of O_2/H_2 = 9 leads to yields of 31.0% and a production of 11.6 µmol-H_2O_2 min^{-1} while O_2/H_2 = 4.5 leads to yields of 62.3% and a production of 22.2 µmol-H_2O_2 min^{-1} at the same partial pressure of H_2 of 0.27 barg.

2.1.2. Influence of flow rate. The variation of flow rate influences the individual mass transfer coefficients, as these coefficients are a function of Reynolds and Schmidt numbers. On the other hand, the liquid flow rate has a linear effect on the liquid residence time, which governs the time in which the catalyst and the dissolved reagents are in contact.

2.1.2.1. Liquid flow rate. The increase of the flow rate has a direct effect on the mass transfer, but also on the concentration of the H_2O_2 produced. It must be considered that the hydrogen gas stream at the inlet was constant. This means that an increase in the production implies the same increase in the yield, as the same H_2 stream is introduced in all cases. The higher flow rate of liquid used dilutes the H_2O_2 being produced, causing a decrease in concentration.

It can be seen in Fig. 2 how for 150 mg 5% Pd/C in 80 mL bed (◊) it is demonstrated that the increase of the liquid velocity (or flow rate) increases the mass transfer and so improves the production. However the effect is not completely independent, as the increase in flow rate causes a decrease of the H_2O_2 concentration and reduces the undesired hydrogenation and decomposition. Also, due to a decrease in the residence time, and depending on the rate of direct synthesis and direct combustion reactions, the final H_2O_2 may change.

To clarify the effect, we made some tests using different amounts of catalyst and bed sizes (runs #04–#13, #58, #62, #66, #70 and #74), as it will be explained later in more detail. For this case, it can be observed that for 75 mg 5% Pd/C in 40 mL bed (○), the production was 125.4 µmol-H_2O_2 min^{-1}, *ca.* 50% higher compared to 150 mg 5% Pd/C in 80 mL bed (◊) of 80.1 µmol-H_2O_2 min^{-1}.

This would mean that, even with half of the quartz bed, the quantity of H_2 transferred would be higher. Nevertheless, it is clear that using a shorter bed, with the same catalyst

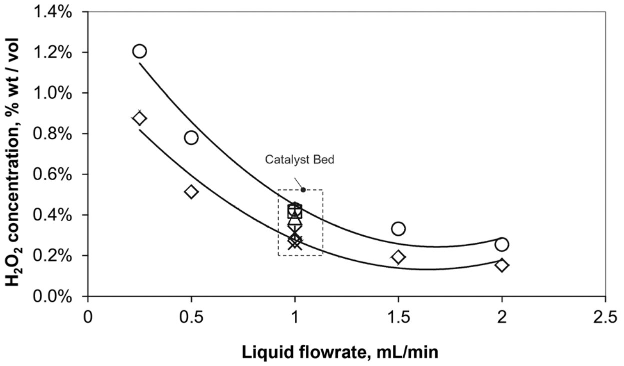

Fig. 3 H_2O_2 concentration *vs.* liquid flow rate for a 5% Pd/C and SiO_2 bed at 28 barg and 25 °C. H_2O_2 production for different catalyst distributions in the trickle bed reactor: (x) 300 mg of Pd/C in 80 mL bed, (◊) 150 mg of Pd/C in 80 mL bed, (*) 100 mg of Pd/C in 80 mL bed, (△) 75 mg of Pd/C in 80 mL bed, (○) 75 mg of Pd/C in 40 mL bed, (□) 50/25 mg of Pd/C in 40/40 mL bed and (+) 37.5/25/12.5 mg of Pd/C in 26.6/26.6/26.6 mL bed.

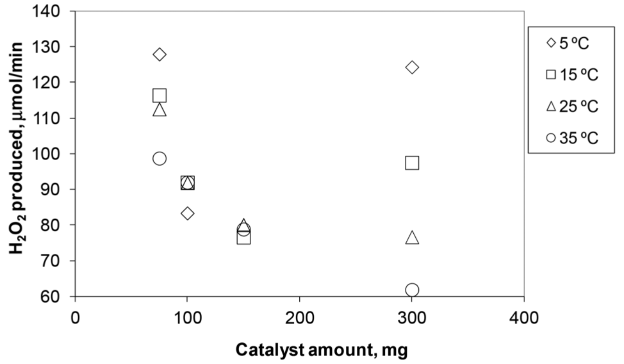

Fig. 4 H_2O_2 production *vs.* catalyst amount in bed, 5% Pd/C and 80 mL SiO_2 bed at 28 barg at 5 °C, 15 °C, 25 °C and 35 °C.

concentration in the bed, the hydrogenation and decomposition of H_2O_2 are considerably suppressed, increasing the efficiency of the process. In this study, we could not measure the H_2 in the off-gas due to experimental limitations, but this experiment confirms the statement. Moreover, using 75 mg of catalyst with 80 mL of quartz, the production was in between the cases just discussed, 112.6 μmol-H_2O_2 min^{-1}, because a larger bed implies more H_2 transferred into the liquid phase and enhanced hydrogenation, too.

Returning to the influence of the liquid flow rate related to the decrease in the H_2O_2 concentration, we can observe that at low flow rates, *e.g.* between 0.25 and 0.5 mL min^{-1} of H_2O, the effect of mass transfer is more pronounced and in Fig. 2 a step change is observed at such a flow rate level, while at high flow rates, the mass transfer effect is less important and the quasi-linear increase in H_2O_2 production can be explained by the H_2O_2 concentration decrease, as shown in Fig. 3.

2.1.2.2. Gas flow rate. The gas flow rate was optimized in previous studies[13–15] with a similar system, so the gas flow rate was kept constant at 4 mL min^{-1} for all the experiments. However, in order to check the influence we carried out two experiments at 2 mL min^{-1} and 4 mL min^{-1} (runs #02 and #03). At low gas flow rates, *i.e.* at 2 mL min^{-1}, the yield was 19.9% and 7.45 μmol-H_2O_2 min^{-1} while at 4 mL min^{-1} the yield was 37.1% and the production 27.8 μmol-H_2O_2 min^{-1}. At low gas flow rates, both the yield and production were lower, indicating that low quantities of H_2 were transferred. A further increase in the gas flow rate may cause bad liquid distribution and bad wetting of the catalyst particles in the TBR, as demonstrated in previous studies, unless the liquid is increased proportionally.[36] Such a hydrodynamic study is out of the scope of this work.

2.2. Kinetic study

2.2.1. Influence of catalyst amount. In the TBR, the inert support acts to increase the surface area for gas transfer into the liquid phase. Nevertheless, the reaction takes place at the surface of the catalyst, *i.e.* at the palladium active sites. Considering the kinetics of the direct synthesis, as has been shown in several studies,[29,37] the number of active sites is included in the reaction rate, mainly considering the first-order influence. For the case of the continuous TBR, the total amount of catalyst is doubly important for: the total number of sites (considering the whole reactor) and also their distribution in the support. The effect of the catalyst concentration on the support and its distribution has not been studied previously, and it is presented in this paper for the first time.

We conducted experiments with four catalyst amounts with 80 mL of SiO_2 support bed (runs #06 and #51–#75) at four temperatures. In general, the increase in the concentration of catalyst in the bed reduces the production at high temperatures (*e.g.* 25 °C and 35 °C), as shown in Fig. 4, which is explained by the increase in the H_2O_2 decomposition and hydrogenation rates.

However, at low temperatures, the effect is not clear, as the production is higher at 75 mg and 300 mg of 5% Pd/C catalyst at 5 °C and 15 °C, respectively. This effect can be explained similarly, considering that at low temperatures the decomposition and hydrogenation are minimized; therefore, increasing the catalyst amount increases these undesired reactions. On the other hand, increasing the catalyst implies more H_2 consumption and more H_2O_2 production, although probably the overall selectivity might decrease, and the production increases again. In this case, the highest production rates were obtained at low temperatures.

2.3. Catalyst and catalyst bed improvement

Following the results obtained with different amounts of hydrogen fed inside the reactor experiments, the amount of hydrogen was kept fixed and the catalyst amount and the catalyst distribution inside the reactor were varied. Experiments were performed with fixed gas flow rate as reported above.

2.3.1. Volume of the support bed. The catalyst was distributed with two different concentrations in the catalyst bed. 150 mg of catalyst were distributed in 100 g of quartz sand and fed inside the reactor and 75 mg of catalyst were diluted in

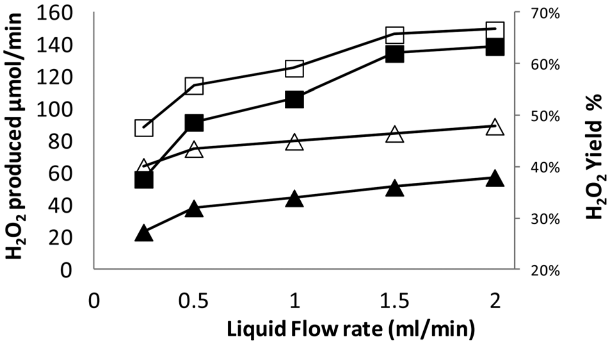

Fig. 5 H_2O_2 production and yield *vs.* liquid flow rate at different supports. (△) H_2O_2 produced and (▲) H_2O_2 yield at 28 barg, 25 °C, 150 mg 5% Pd/C/80 mL quartz sand, (□) H_2O_2 produced and (■) H_2O_2 yield at 28 barg, 25 °C, 75 mg 5% Pd/C/40 mL quartz sand.

50 g of quartz sand and fed into the reactor (to fill completely the reactor in the latter case 50 g of quartz sand were used). Experiments were performed at 25 °C varying the liquid flow rate and keeping constant the gas flow rate at 4 mL min^{-1}. The results are illustrated in Fig. 5.

The temperature, pressure and gas flow rate were kept constant and the only parameter changed during the experiments was the liquid flow rate. An increase in the liquid flow rate always corresponds to an increase on the production of hydrogen peroxide as can be seen. The increase of H_2O_2 production is more pronounced in the range between a liquid flow rate of 0.25 and 1 mL min^{-1}, while between 1 and 2 mL min^{-1} the increase is less pronounced but still remarkable. It seems that a plateau is not reached, meaning that there is a possibility to further enhance the production of H_2O_2. The fact that an increasing liquid flow rate increases the quantity of H_2O_2 is probably due to two factors: (1) the mass transfer of hydrogen is increased with increasing the liquid flow rate; more H_2 reacts to produce more water or hydrogen peroxide; (2) hydrogenation and decomposition of H_2O_2 are decreased due to the lower contact time of the liquid phase with the catalyst. The same trend can be found in the results related to the yield of H_2O_2 (solid black triangles), where the yield constantly increases with the liquid flow rate. The simultaneous analysis of both the results of the production and the yield of H_2O_2 seems to confirm the two hypotheses made above. A confirmation of the hypothesis made above originates from the results obtained halving the catalyst bed in the trickle bed. The experiments conducted with 75 mg of active catalyst and 40 mL of quartz sand showed the same trend as the previous experiment with 150 mg of catalyst in 80 mL of quartz sand. Interestingly, the production of H_2O_2 and the yield were higher compared to the former experiments. These results can be explained with the fact that H_2O_2 is less hydrogenated as the reaction is performed in the bed with less catalyst. Usually when the quantity of the catalyst is diminished, the amount of the products is less. For the hydrogen peroxide direct synthesis that counts parallel and consecutive reactions, the results are the opposite. The lower the catalyst amount the higher is the production of hydrogen peroxide, probably due to some factors: (1) when the residence time in the catalytic bed is the lowest, subsequent hydrogenation and decomposition of hydrogen peroxide affect less the direct synthesis; (2) the H_2/Pd ratio plays an important role in the subsequent hydrogenation after the H_2O_2 formation.

2.3.2. Concentration distribution of the catalyst in the support bed. Following the results with low catalyst amounts and considering that the H_2/Pd ratio plays an important role in the direct synthesis, three different catalyst bed arrangements were designed and charged into the trickle bed reactor to confirm the hypothesis reported above. Bed (A) consisted of 75 mg of catalyst uniformly distributed in 80 mL of quartz sand, while bed (B) was composed of 40 mL of quartz on the bottom with 25 mg of catalyst perfectly mixed together and above that 50 mg of catalyst dispersed in 40 mL of quartz sand and, finally, bed (C) was divided into three parts of 26.6 mL of quartz sand and from the bottom the quantity of the catalyst was 12.5, 25 and 37.5 mg in each part of the quartz sand. Visual distribution of the catalytic bed is reported in Fig. 6. First of all, the concentration of hydrogen peroxide at the outlet and the yield of H_2O_2 decreased linearly with increasing the temperature.

The idea was developed to confirm that there is an optimum H_2/Pd ratio and if it is kept constant or above some values (without decreasing it too much), hydrogenation can be suppressed. The results in Fig. 7 confirmed our hypothesis that working with a gradient of the catalyst concentration along the bed can lead to an enhancement on both production and yield of H_2O_2. The results showed that bed (C) (empty triangles = production of H_2O_2, solid black triangles = yield%) was the one giving the best results followed by bed (B) (empty squares = production of H_2O_2, solid black squares = yield%) and bed (A) (empty diamonds = production of H_2O_2, solid black diamonds = yield%). From those preliminary results from bed (A) to bed (C), there is an average enhancement of 10% in the yield and of 20 µmol min^{-1} of H_2O_2 produced only with a different disposition of the catalyst bed. The best result was found at 5 °C, as the yield was improved by a value of 10% from 50% with bed (A) to 60% with bed (C). The production rate was 130 µmol min^{-1} with bed (A) and 150 µmol min^{-1}

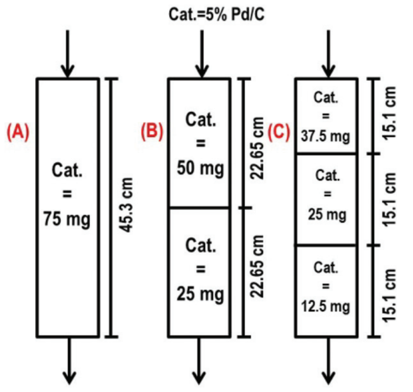

Fig. 6 Visual distribution of the catalytic bed.

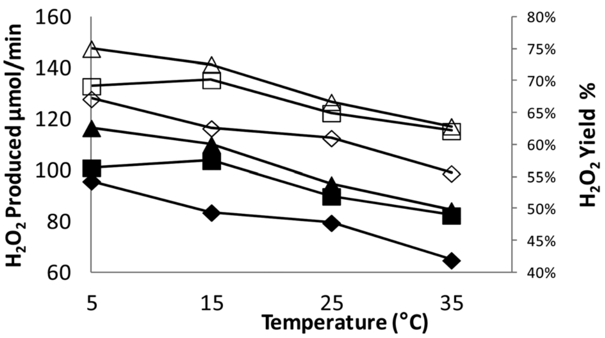

Fig. 7 H_2O_2 production and yield *vs.* temperature at different catalyst concentrations in the bed support with 4 mL min^{-1} gas flow rate and 1 mL min^{-1} liquid flow rate: (△, ▲) H_2O_2 produced and yield at 28 barg 5% Pd/C : quartz sand = 75 mg : 80 mL, (□, ■) H_2O_2 produced and yield at 28 barg 5% Pd/C : quartz sand = 25 and 50 mg : 40 and 40 mL, (◊, ◆) H_2O_2 produced and yield at 28 barg 5% Pd/C : quartz sand = 12.5, 25 and 37.5 mg : 26.6, 26.6 and 26.6 mL.

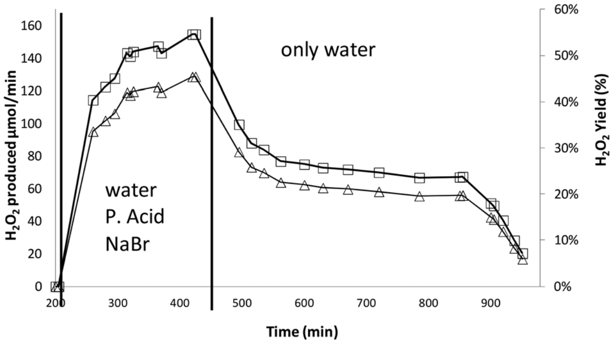

Fig. 8 H_2O_2 production and yield *vs.* time at different unsteady Br-inlet concentrations: (△) H_2O_2 produced and (□) H_2O_2 yield at 28 barg, 25 °C, 5% Pd/C : quartz sand = 12.5, 25 and 37.5 mg : 26.6, 26.6 and 26.6 mL.

with bed (C). The amount of the active catalyst was the same and if the hydrogenation was not influenced by the local H_2/Pd ratio, the results should have been exactly the same. These results showed that the hypothesis made was correct because with this different disposition, the hydrogenation is kept lower in bed (C) than in bed (A). All the results obtained with bed (B) were showing the same trend as in the former cases: the decreasing of the production and yield of H_2O_2 when the temperature was increased.

2.3.3. Bromide concentration.

Bromide plays an important role in the direct synthesis, but its effect on the reaction is still not completely understood. The experiments were performed with the same catalyst bed that gave the most promising results (*e.g.* three parts of 26.6 mL of quartz sand and from the bottom, the quantity of the catalyst was 12.5, 25 and 37.5 mg in each quartz sand portion). The experiment was conducted as follows: the feeding was only water until 220 minutes, then it was switched to the mixture water + acid + NaBr until 450 minutes and then again to water alone; the results are shown in Fig. 8.

No H_2O_2 was detected at the outlet when the feeding was only water. This implicates two possibilities: (1) there is no direct synthesis if the bromide and the acid are not present in the reacting medium; (2) the reaction happens, but the subsequent formation of water is faster and the result is that all H_2O_2 produced is converted into water. Studies in a different reactant medium are needed to identify which one of the possibilities is the real one. Suddenly, when the feeding was switched to the reactant medium mixture (*e.g.* water + acid + NaBr), the production of H_2O_2 is remarkable and reaches the maximum value after 120 minutes, *i.e.* the same value of H_2O_2 in terms of production and yield obtained in another experiment with the same disposition of the catalyst bed (excellent reproducibility). After we confirmed that, with the reaction medium mixture we used for all experiments, it is possible to obtain reproducible results, the feeding was again switched to pure water and H_2O_2 production and yield were halved in 50 minutes. The real surprising result was that the H_2O_2 production and yield remained constant for around 400 minutes without any additives. After that (at 850 minutes) both the H_2O_2 production and yield decreased faster. To understand the activity reported above, palladium and bromide concentrations were analyzed during all the experiments and coupled with H_2O_2 production rate results. ICP measurements for Pd and Br^- revealed the presence of 330 ppm of bromide and 0.46 ppm of palladium at the outlet in the presence of an acidic–bromide solution. However when the feeding of the acidic–bromide solution was stopped, a concentration of 5 ppm min^{-1} of Br- or lower and 0.017 ppm of Pd was coming out from the outlet. The value of 5 ppm represents around 1.5% of the bromide fed inside the reactor when the experiments were in the acidic–bromide feeding zone. This means that when the acidic solution is fed into the reactor, there is probably an adsorption of the bromide on the carbon and on the inert particles (SiO_2) surface. When the acidic–bromide solution feeding was stopped, probably the bromide adsorbed on the catalyst surface (and inert particle surface) was slowly released, maintaining with its effect some of the catalytic properties of the palladium to produce hydrogen peroxide. A detailed analysis of the palladium and bromide concentrations at the outlet of the reactor is reported in Fig. 9.

From the results analysis, it can be said that the Pd leaching is promoted by the bromide and the acid contained in the reaction liquid mixture. In the experiment zone where the bromide–acidic solution was fed, a total amount of 0.1 mg of

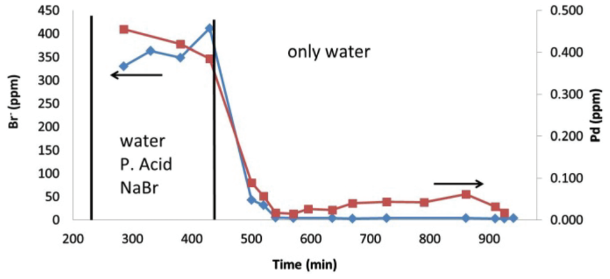

Fig. 9 Palladium (■, red) and bromide (◆, light blue); the same conditions of the experiment reported in Fig. 8.

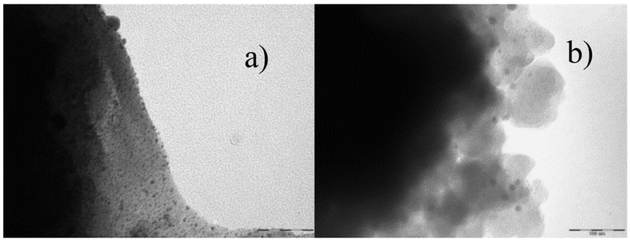

Fig. 10 TEM images of the fresh catalyst (a) and spent catalyst (b); focus 160 K.

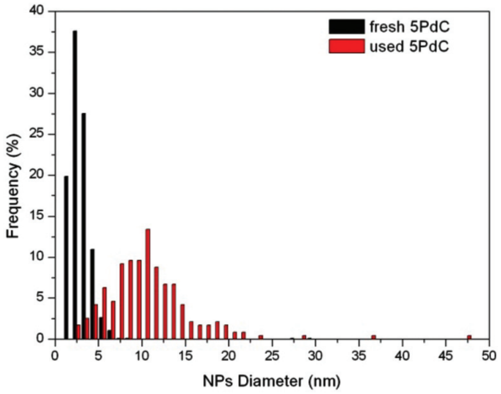

Fig. 11 Palladium nanocluster diameter before and after the direct synthesis.

Pd leached from the catalyst. The catalyst lost 2.5 wt% of Pd in around four hours. After the bromide–acidic solution was stopped, Pd leaching was almost zero (0.2%) in 8 hours. It is worth mentioning that previous calculation studies showed that a pretreatment with acids and halides weaken the interaction between the metal surface and the reagents (*i.e.* changing the metal surface of the palladium cluster with the leaching).[38]

The TEM analysis revealed how the palladium nanocluster diameter changed during the reaction (Fig. 10). Fig. 10a represents the catalyst before the reaction and Fig. 10b represents the catalyst after the reaction. A sintering effect is shown in Fig. 10b compared to Fig. 10a.

It is interesting to notice from the TEM analyses (Fig. 10 and 11) how the distribution of the Pd nanoparticles changed: the average diameter before the reaction was around 3 nm with a narrow distribution and that after the reaction was around 12 nm with a broad distribution. The results of the ICP and TEM analyses allow for some considerations. It is clear that the bromide–acidic solution (and probably the H_2O_2 formed during the reaction) modifies the palladium nanoparticles. The leaching of the palladium happened mostly when bromide and acid are in the solution fed. Under these conditions, the hydrogen peroxide formed reached the maximum production rate of all the experiments (Fig. 8 and 9). The interesting part of the experiment was the second half: when the bromide–acidic solution was substituted with water, the H_2O_2 production rate was halved (Fig. 8 and 9). The bromide and palladium concentrations after only water had been fed were very low (5 ppm of bromide and 0.0166 ppm of palladium), but the hydrogen peroxide production rate at the outlet was still remarkable.

From the results depicted in Fig. 9, we have estimated that running a reaction using 7.5 mg of Pd (*e.g.* 150 mg of 5% Pd/C wt catalyst) using promoters, the palladium will leach in approx. 10 days (considering 0.5 ppm and 1 mL min^{-1}), while if no promoters were used it would take *ca.* 100 days (considering 0.05 ppm and 1 mL min^{-1}). We must recognise that the productivity is a function of the promoter concentration, but a convenient selection of the promoter concentration, target productivity and amount of catalyst can provide a workable process. The non-steady state operation of promoters can be key to operating the process at maximum efficiency.

The ICP and TEM results coupled together construct the idea that the bromide acted as a palladium nanoparticle modifier with two effects. The first effect was a surface restructuration of the palladium nanoparticles making them more effective for the direct synthesis. The second effect was the sintering of the palladium nanoparticles (an effect noticed also in the other experiments with only acidic–bromide feeding).

The first effect was probably the most important. The interpretation of the data led to the supposition that the surface restructuration was reversible: when the solution contained phosphoric acid and bromide, we have one palladium surface structure, whereas when the fed did not contain the promoters we have another palladium surface structure. When the surface was similar to the initial state (fresh catalyst), no hydrogen peroxide could be detected. A possible speculation can be that bromide interacts with some palladium sites, promoting the palladium leaching and influencing the surface structure, enhancing in this way the direct synthesis. When the acidic–bromide solution was substituted with water the surface went back to the initial (and thermodynamically favoured) structure. A drawback of the acidic–bromide solution was the quite significant leaching of the palladium (measured using ICP-MS). Nevertheless, these discoveries can help to identify new reaction conditions and can contribute to the development of a new catalyst. Different experiments are needed to identify the real effect of the bromide in the direct synthesis. Catalytic properties need to be investigated during all of the transient experiment performed, not only at the beginning or at the end of the experiment. Catalyst pretreatment is probably a tool that has to be investigated deeply to understand how the direct synthesis can be improved with this new method.

2.4. Optimization guidelines

As demonstrated in this research, the production of H_2O_2 in continuous mode is a feasible alternative using a TBR. The key outcome variables are the H_2O_2 molar flow production, the concentration of H_2O_2, the total H_2 conversion and selectivity. In this work, due to experimental limitations, we have not measured conversion and we have inferred the selectivity through the analysis of the yield. Although it does not give the same information, it is enough to understand the system and the extract conclusions on how to optimize it.

First, as can be seen, the maximum productivity (run #13, 149.4 μmol-H_2O_2 min^{-1}), yield (run #48, 74.1%) and H_2O_2 concentration (run #09, 1.205% wt) were obtained with 75 mg 5% Pd/C and 40 mL bed. This implies a recommended concentration to be used of *ca.* 0.1 mg-Pd mL^{-1}-bed that, for the quartz sand bed used in this case (0.2–0.8 mm particle size), can be estimated as between 3.2 and 12.7 mg-Pd m^{-2}-surface area of the bed.

Second, the maximum productivity and the maximum concentration were obtained at the maximum pressure screening, *i.e.* 28 barg (P_{H_2} = 1.16 bara) and 25 °C, while the critical parameter in this case was the liquid flow rate. Furthermore, high liquid flow rates implied the maximum productivity of 149.4 μmol-H_2O_2 min^{-1}, because of a combination of increased mass transfer and decreasing H_2O_2 concentration (0.254% wt) therefore decreased the decomposition/hydrogenation effect, while, on the other hand, the maximum concentration of 1.205% wt was obtained at 0.25 mL min^{-1} of liquid, with only 88.6 μmol-H_2O_2 min^{-1} produced. However, as it can be seen between these two experiments, the increase in the concentration from 2 mL min^{-1} down to 0.25 mL min^{-1} was about 370%, while the decrease in production was only 41%. According to our preliminary simulations, in order to compare the energy requirements, to concentrate the H_2O_2 produced from 0.254% or 1.205% wt to a value of 10% or 30% wt, the energy flows, both cooling and heating up, are comparable for each starting concentration (as shown in Table 2 and Fig. 12). In fact, concentrating the H_2O_2 from 0.254% wt requires 10–11% more energy in cooling and heating than starting from 1.205% wt. This means that the final optimization must be a compromise between the costs of H_2 consumed, the molar flow of H_2O_2 produced and the energy requirements.

Third, in terms of yield, better yields were obtained as the inlet flow rate of H_2 was balanced with the concentration of H_2O_2 obtained and most of the H_2 was used in the reactor to produce H_2O_2, but not to hydrogenate it. Mainly, yields over 60% coincide with the low and medium pressures in this system. This confirms that it is really important to keep the maximum H_2O_2 value below a certain value of *ca.* 0.2–0.3% wt to minimize this undesired side reaction and maximize the production. There are two exceptions: first, runs #12 and #13, where 28 barg and high liquid flow rates were used (*i.e.* 1.5 and 2 mL min^{-1} respectively), where the yields reached 62.1 and 63.4% respectively; second, runs #72 and #73, where 28 barg and low catalyst densities were employed.

Table 2 Simulated heat flows for the distillation of H_2O_2[a]

H_2O_2 inlet conc. (% wt)	H_2O_2 final conc. (% wt)	Heat flow condenser (kJ kg^{-1})	Heat flow subcool (kJ kg^{-1})	Heat flow total cond. (kJ kg^{-1})	Heat flow reboiler (J kg^{-1})
0.254%	10.0%	−4868	−540.0	−5408	5435
0.254%	30.0%	−4953	−549.4	−5502	5524
1.205%	10.0%	−4390	−486.7	−4877	4928
1.205%	30.0%	−4794	−531.7	−5326	5356

[a] The simulation has been carried out using Aspen Plus ONE7.1, the distillation was carried out in a 12 theoretical stages RadFrac column at 0.6 barg condenser with subcooling temperature of 35 °C and thermodynamic property package Peng–Robinson.

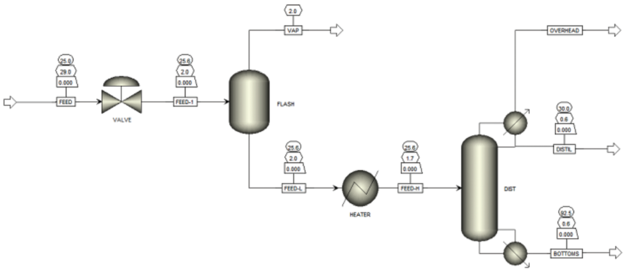

Fig. 12 H_2O_2 flow sheet for concentration of H_2O_2 using Aspen Plus ONE 7.1.

Fourth, considering reaction temperature, direct synthesis can work between 10 and 60 °C as we have demonstrated in this paper and many authors have proven before. Working below 30 °C is not recommended from an industrial point of view as it would be difficult to remove the heat produced in the reaction (*i.e.* a low temperature utility is expensive). Nevertheless, working between 40 and 60 °C is affordable. These temperatures are used also in traditional synthesis.

Finally, drafting an energy requirement, in both traditional and direct synthesis vacuum distillation is needed, so similar levels of energy consumption are expected between both processes. However, the use of an organic solvent or the use of methanol (for direct synthesis) can sometimes simplify the distillation (as they have lower boiling points) but they comprise a high number of distillation columns required in series, as many side products are formed (from the oxidation of the organics).

3. Conclusions

A down-flow trickle bed reactor was set up to perform hydrogen direct synthesis continuously over a 5% Pd/C catalyst. The reaction conditions were changed in order to maximize the hydrogen peroxide production. The catalyst was uniformly diluted in quartz sand in different concentrations to investigate their effects on the direct synthesis. The amount of catalyst and the distribution of the catalyst along the bed were optimized to obtain the highest possible yield. The distribution of the catalyst along the bed gave the possibility to significantly improve the yield and the production of hydrogen peroxide (up to 65% and 0.5% w/w respectively). This configuration with a gradient of the catalyst concentration from the top to the bottom in the reactor gave important results and information on the H_2O_2 direct synthesis. Higher production rates and yields were obtained as the catalyst concentration decreased along the bed from the top to the bottom compared to the uniformly dispersed catalyst. The H_2/Pd ratio was found to be an important parameter that has to be investigated in the hydrogen peroxide direct synthesis. The effect of a pretreatment of the catalyst with a solution of sodium bromide and phosphoric acid was studied; the results showed how a catalyst pre-treatment can lead to an improvement of the direct synthesis of hydrogen peroxide in water, especially by controlling the leaching of palladium and by the use of promoters to increase selectivity.

The combination of catalyst development and chemical reaction engineering is a key point to successfully understand/improve the hydrogen peroxide direct synthesis. The catalyst gradient along the reactor and the catalyst pre-treatment are new ideas to improve hydrogen peroxide direct synthesis by controlling the ratio of H_2–H_2O_2 and H_2–active metal along the reactor. Hydrogen peroxide direct synthesis was improved with these non-conventional experiments and reactor design. Optimization guidelines were provided in order to increase the hydrogen peroxide production.

4. Experimental section

4.1. Materials and methods

4.1.1. Materials. For this research the catalyst was microparticles of an activated carbon support with an average of 5 wt% Pd (2 to 5 nm size) purchased from Degussa. The catalyst powder was weighed and mixed homogeneously with SiO_2 particles creating a catalytic bed.

Deionised water was used as the reaction solvent. NaBr (Flucka) and H_3PO_4 (Sigma-Aldrich) were used as H_2O_2 promoters dissolved in the water inlet stream. SiO_2 microparticles of 150–200 μm (Sigma-Aldrich) were used as the trickle bed inert support. Potassium iodide, H_2SO_4, $Na_2S_2O_3{\cdot}5H_2O$ 99.5%, starch from Sigma–Aldrich and $K_2Cr_2O_7$ (Riedel de Haën) were used for titration analysis.

4.2. Methods

H_2O_2 concentration in H_2O was determined using iodometric titration. The yield was calculated as H_2O_2 produced in mmol min^{-1} divided by H_2 entering the reactor in mmol min^{-1}.

TEM specification: energy-filtered transmission electron microscopy (EFTEM, LEO 912 Omega, acceleration voltage of 120 kV, LaB6 filament).

The determination of Pd and Br has been done using an ICP-MS instrument, a PerkinElmer Sciex and an ICP Mass Spectrometer 6100 DRC Plus. The analysis was conducted using the quantitative standard mode. The timing parameters were: Sweeps/Reading: 11, Readings/Replicate: 1, the Number of Replicates: 7, Dwell time: 50.0 ms, Scan mode: Peak Hopping. The calibration solutions have been prepared from a commercial single element solution for both Pd and Br, diluted into standard serial from 1 ppb to 100 ppb.

4.3. Experimental apparatus

The system consists of four sections: liquid inlet, gas inlet, three-phase reaction and biphasic separation. The liquid was pumped at room temperature using an HPLC pump (P-01). The gases were fed independently from gas cylinders (D-02 with CO_2/H_2 97.5/2.5 mol%, or CO_2/H_2 95/5 mol% and D-03 with pure O_2) controlled by mass flow controllers (FCV-01 and FCV-02 respectively). Volumetric flow rates reported in the figures and tables were estimated using mixture densities determined with the Redlich–Kwong–Soave with the Boston–Mathias modification thermodynamic package in Aspen Properties software.[35]

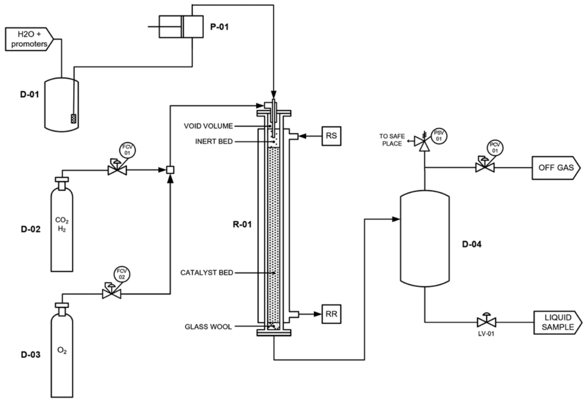

Fig. 13 Schematic flow diagram of the trickle bed reactor (TBR) system; D-01 = water and promoters inlet vessel, P-01 = HPLC pump, D-02 = H_2 + CO_2 cylinder, D-03 = O_2 cylinder, D-04 = liquid product collecting vessel, FCV-01 = gas flow controller, FCV-02 = gas flow controller, LV = liquid sampling valve, R-01 = TBR (RS = refrigerant supply, RR = refrigerant return).

The TBR was made of AISI 316 stainless steel (Fig. 13), 60 cm long and 1.5 cm I.D. (*ca.* 105 mL) passivized using nitric acid 30% wt during 4 hours to prevent H_2O_2 decomposition due to iron catalysis. The bed was composed of 2 cm of glass wool at the bottom and up to 110 g of quartz sand (*ca.* 80–100 mL). The reactor accommodated a catalyst bed up to 60 cm long. The reactor operates in continuous co-current gas and liquid. The TBR operates in isothermal mode between −20 °C and 60 °C by controlling the temperature through a heating–cooling jacket. The temperature inside the reactor was measured with a K thermocouple after the initial mixing zone in the bed. The pressure inside the reactor was controlled using a back pressure automatic controller installed at the off-gas outlet (PCV-01). A rupture disc was installed for safety reasons in the off-gas line. The liquid entrance was inserted inside the bed, so that the quartz acted as a liquid distributor. It is extremely important to start up the TBR at low liquid flow rates ensuring proper wetting of the bed. The gas entered into a small void volume (*ca.* 3 mL) acting as pressure compensator and gas distributor. A manual globe valve was used to sample the instantaneous liquid phase.

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