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Continuous H₂O₂ direct synthesis process: an analysis of the process conditions that make the difference

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Abstract: A trickle bed reactor (TBR) was used to study different process parameters upon hydrogen peroxide direct synthesis. The catalysts used were commercial palladium on active carbon. The influence of pressure (1.75–25 barg), temperature (5–60°C), liquid flow rate (2–13.8 ml·min⁻¹), gas flow rate (3.4–58.5 ml·min⁻¹), catalyst amount (90–540 mg), Pd percentage on the support (5% wt., 10% wt. and 30% wt. Pd/C) as well as promoter concentrations (0.0005–0.001 M) were all varied as process parameters to better understand the behaviour of the system. By contrast, the gas phase molar composition of the feed (4:20:76=H₂:O₂:CO₂) was kept constant. The strong influence between liquid flow rate, gas flow rate and catalyst amount were identified as the key parameters to tune the reaction, and related to the activity of the catalyst. In essence, these parameters must be carefully tuned to control the hydrogen consumption. The maximum productivity (289 μmol H₂O₂·min⁻¹) and yield (83.8%) were obtained

when a diluted bed of 30% Pd/C was applied. The H₂O₂ hydrogenation was studied in order to understand its role in the H₂O₂ direct synthesis reaction network. The hydrogenation reaction mechanism and the role of NaBr were identified thanks to the experiment proposed in the present work. Consequently, understanding the whole reaction mechanism from the process conditions studied led to a deeper understanding of all of the phenomena involved in the H₂O₂ direct synthesis.

Keywords: direct synthesis; heterogeneous catalysis; hydrogen peroxide; palladium on carbon; trickle bed reactor.

1 Introduction

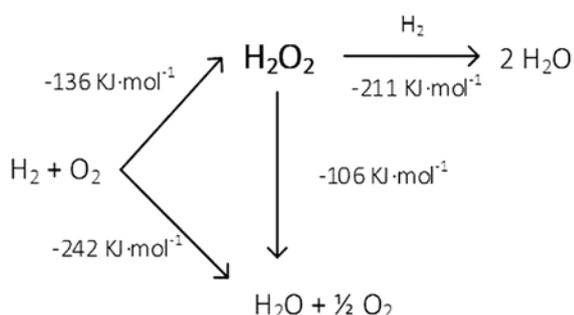
The chemical industry and society have been looking for new and more sustainability products and processes for decades. One of the most used commodity chemical products is hydrogen peroxide, with a wide range of applications primarily as an oxidant, from paper to electronic industries. Its demand increases year after year and annual market is close to 3000 kt/y [1]. In fact, the traditional synthesis route, auto-oxidation process, is used to produce more than 95% of the total production. However, it is not capable to conform to the new “green” market demands, strongly related to formation of byproducts and application of energy-demanding purifying stages [2, 3]. Moreover, H₂O₂ direct synthesis can be the future of processes to produce electronic grade chemicals [4]. A viable alternative to this large scale process for a smaller scale can be the direct synthesis, due to its green philosophy and the clean byproducts produced (Scheme 1). Direct synthesis of H₂O₂ is a three phase reaction process encompassing by a one desired reaction, hydrogen peroxide synthesis, and three undesired reactions, water synthesis, H₂O₂ decomposition and H₂O₂ hydrogenation (Scheme 1). The main problem of the direct synthesis, apart from the safety concerns on the H₂/O₂ mixtures, is the selectivity.

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Scheme 1: H₂O₂ direct synthesis reaction scheme.

The challenge is that usually the catalysts active for the direct synthesis are also active for the H₂O formation and for the H₂O₂ hydrogenation.

Undesired reactions can be minimized by different approaches. The main issue is still the design of appropriated catalysts [5] (active metal or support [6–17]), followed by the focus on the addition of promoters (acids and halides) [6, 11, 16, 17], selection of liquid solvent (water, methanol, ethanol or a mixture of them) and optimization of reaction conditions since appropriate selection of operational parameters are crucial in aiming at high selectivities in the H₂O₂ direct synthesis [18–29]. Finally, the gas phase concentration is limited by flammability limits of hydrogen–oxygen mixtures. An inert gas, typically CO₂ or N₂, is needed to maintain the H₂ concentration below the lower flammability limits (3.6–4.0%).

Hydrogen peroxide direct synthesis could compete with traditional auto-oxidation process only if the process will be able to produce a clean solution of H₂O₂ close to a concentration of 12–15% wt. [29].

The direct synthesis of H₂O₂ in water over a solid catalyst is a three phase reaction and thus it is beneficial to use a flow-through reactor that allows continuous H₂O₂ production. An appropriate contacting between three phases (solid-liquid-gas) is important to minimize the mass transfer limitations. One of the most promising reactors for the

H₂O₂ direct synthesis is a trickle bed reactor (TBR). Henkel and Weber [30] patented one of the first TBRs for hydrogen peroxide direct synthesis. Following this idea, only recently, the TBRs were studied for the H₂O₂ direct synthesis [18–21]. However, it is not only important to study the reactor itself, but also the reactor-catalyst system. As an example, the effect of the catalyst supports (a commercial cross-linked polymeric matrix and sulphated zirconia) in terms of the selectivity of palladium catalyst were evaluated in the TBR, the reaction medium was methanol and the selectivity obtained was around 70% [20]. Furthermore, the influence of gas phase molar ratio was also studied (methanol as reaction medium) with a promising bimetallic catalyst (Pd-Au), and the selectivity obtained there was around 90% [21]. Direct synthesis reactions have also been studied using water as the liquid phase with a 5% Pd/C and a mixture of sodium bromide/phosphoric acid as promoters [18]. The most important parameters studied were pressure (5–28 barg), liquid flow rate (0.25–2 ml·min⁻¹), amount of catalyst (30–300 mg) and the total distribution of solid along the reactor. It was concluded that the system performance can be optimized by an appropriate selection of catalyst distribution, trying to maintain a high H₂/Pd ratio beneficial upon H₂O₂ direct synthesis.

Heterogeneous catalysed reactions are complex and their understanding and optimization require exhaustive investigations of the operational parameters and reaction mechanism, especially for H₂O₂ direct synthesis [31, 32]. Indeed, the behaviour of the system can be used to design more efficient catalysts. Moreover, if only one parameter is studied, the results are applicable only for the conditions proposed. Other studies involving the direct synthesis in a continuous reactor are shown in Table 1.

The aim of this work was to study different process conditions for the H₂O₂ direct synthesis and to give useful guidelines in terms of the reaction conditions and product distribution to maximize catalysts performances with different Pd/C catalysts. Moreover, here we wanted to clarify

Table 1: Performance comparison of different reactor systems.

Reference	Reactor type	Catalyst	Temperature	Pressure	Solvent	H ₂ O ₂ Productivity ^a
Present work	TBR	5% Pd/C	288	28	H ₂ O+acid+bromide	2000
Paunovic et al. [33]	Microreactor	5% AuPd/SiO ₂	303	20	H ₂ O+acid+bromide	3500
Freakley et al. [22]	Millireactor	1% PdAu/TiO ₂	275	10	66% MeOH+34% H ₂ O	400
Inoue et al. [34]	Microreactor	5% PdAu/TiO ₂	293	10	H ₂ O+acid+bromide	3000
Biasi et al. [18]	TBR	5% Pd/C	288	28	H ₂ O+acid+bromide	1120
Kim et al. [24]	Upflow	0.24% Pd/resin	295	50	MeOH+acid+bromide	5300

^amol H₂O₂·kgPd⁻¹·h⁻¹.

TBR, Trickle bed reactor.

the effect of NaBr on the catalyst activation step for the H_2O_2 direct synthesis and consequently the mechanism behind the hydrogenation reaction. Hereby, we report, in an objective way, what is important to understand and analyse to control the H_2O_2 direct synthesis from the operational point of view.

2 Materials and methods

2.1 Materials

The TBR bed was composed of a mixture of Pd/C catalyst and SiO_2 . SiO_2 microparticles (200–500 μm Sigma-Aldrich Finland Oy, Helsinki, Finland) were used as inert material to dilute the catalyst and increase the mass transfer area of the reactor. The active catalyst was carbon with 5%, 10% and 30% of Pd (Sigma-Aldrich Finland Oy, Helsinki, Finland) used without any further modification. Glass wool (from Carl Roth, Tampereen Penli OY, Ylöjärvi, Finland) was used as plugs inside the reactor to immobilise the SiO_2 -Pd/C mixture. Hydrogen peroxide concentration in the reaction was measured by iodometric titration. For the iodometric titration, potassium iodide (99.5%, Sigma-Aldrich Finland Oy, Helsinki, Finland), sulphuric acid (98%, J.T. Baker, VWR International Oy, Helsinki, Finland), starch (Merck Oy, Espoo, Finland), sodium thiosulfate pentahydrate (99.5%,

Sigma-Aldrich Finland Oy, Helsinki, Finland) and ammonium molybdate tetrahydrate (99.0%, Fluka) were used as reagents. All of the experiments were carried out using deionized water as the reaction medium. To minimise hydrogenation and decomposition, promoters were used: phosphoric acid (99.0%, Sigma-Aldrich Finland Oy, Helsinki, Finland) and sodium bromide (99.5%, Sigma-Aldrich Finland Oy, Helsinki, Finland). Premium grade (99.999%) oxygen (O_2), nitrogen (N_2) and hydrogen/carbon dioxide (H_2/CO_2) were supplied by AGA Oy (Linde Group, Finland).

2.2 Experimental set-up

The experimental set-up used for the experiments was quite similar to the system used in a previous work [18]. Briefly, the reactor was made of AISI 316 stainless steel, 60 cm long and with an internal diameter of 1.5 cm. The reactor was passivized with 30 wt./wt.% HNO_3 overnight to minimise hydrogen peroxide decomposition. Figure 1 shows the complete apparatus.

2.3 Methods

Reaction progress was measured and controlled by measuring hydrogen peroxide concentration in the liquid phase, while oxygen and hydrogen were monitored in the gas phase. H_2O_2 concentration was determined by iodometric titration. The influence of pressure,

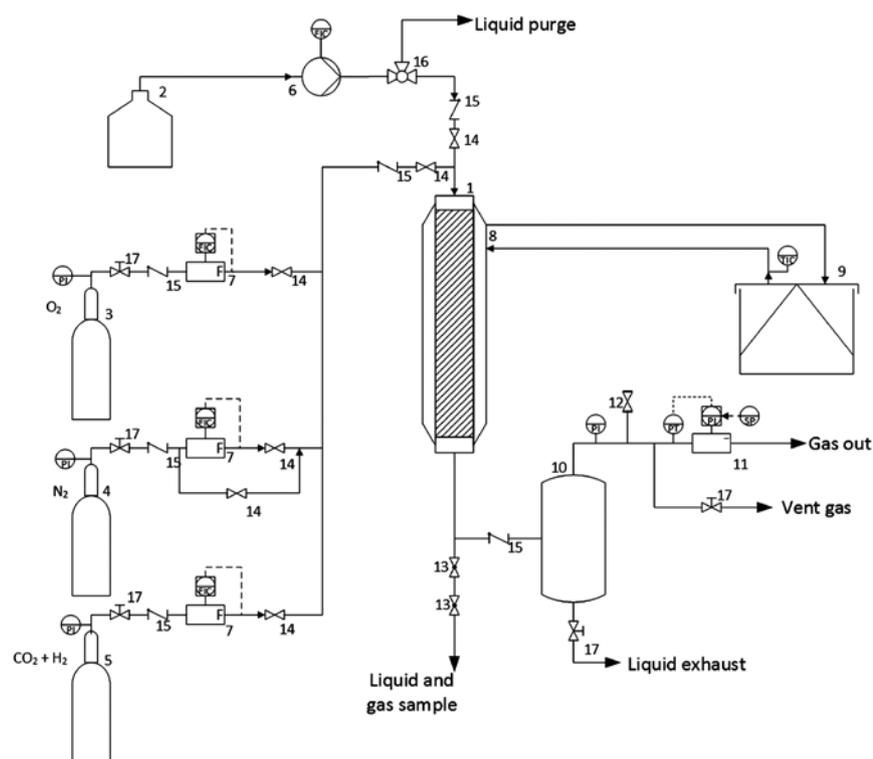


Figure 1: Scheme of the apparatus used in the H_2O_2 experiments. (1) Trickle bed reactor. (2) Liquid solvent supply. (3, 4, 5) Gas bottles, O_2 , N_2 and CO_2/H_2 (95/5%). (6) Pump. (7) Mass flow controller. (8, 9) External cooling and chiller with temperature controller. (10) Liquid collection vessel. (11) Pressure controller. (12) Vent valve. (13) Micrometric valve. (14) On/off valve. (15) Check valve. (16) Three-way valve. (17) Ball valve.

temperature, liquid flow rate, gas flow rate, amount of catalyst and palladium catalyst percentage in a TBR with a high L/D ratio were monitored. The experimental conditions are summarized in Supplemental Table 1 (in the supplemental material) and the summary of the results are reported in Supplemental Table 2 (in the supplemental material). Gas composition was constant 76/20/4% mol (CO₂/O₂/H₂). Volumetric gas flow rate may vary according to temperature and pressure values in order to ensure constant molar gas flow rate. Monitoring the molar gas flow rate constant simplified the study and the comparison of the final results. Oxygen to hydrogen molar ratio (O₂/H₂) was fixed at around 5, according to the earlier conclusions that suggest that an excess of O₂ can minimize the sites devoted to the production of water [8].

Hydrogen peroxide production rate ($F_{H_2O_2}$) and turnover frequency values were calculated from H₂O₂% wt/v concentration in liquid phase. Yield was defined as the moles of hydrogen peroxide produced divided by the moles of hydrogen fed into the reactor (percent yield=actual yield/theoretical yield). Hydrogen concentration on gas phase at the outlet of the reactor was negligible (i.e. around 100% of H₂ conversion).

2.4 Experimental procedure

The reactor was filled with a mixture of catalyst and quartz sand corresponding to each experiment. Care had to be taken upon reactor loading avoiding any empty spaces and assuring a homogeneous catalyst concentration along the bed. To start the reaction, the desired pressure was attained by N₂, followed by pumping of liquid for 30–60 min to ensure complete wetness of the catalytic bed. Correspondingly, the liquid and gas flow rate values were then adjusted as desired. During the actual experiment, gas and liquid samples were withdrawn every 15 min after the reactor started to operate in steady state regime.

3 Results and discussion

In TBRs there is the possibility to work under six different flow regimes [35]. A low liquid flow rate and a low gas flow rate are generally desired for trickle bed operations. This ensures low gas-liquid interactions and liquid flows around solid particles as a film or rivulets. However, the industrial scale and laboratory scale do not necessarily behave in the same way or follow the same physical rules. At industrial scale, gravity acts as the main force, while capillary forces are the main ones at laboratory scale. Eötvös number ($E\ddot{o}$ =gravitational force/capillary force) calculated for this experimental system had small values (0.006–0.012) which confirms that capillary forces have a great influence over behaviour of the hydrodynamic system [36]. The influence of the capillary force could be moderated by the high length-diameter reactor ratio (L/D=40), although that effect cannot be directly measured since it is not

included in the Eötvös number. In fact, not many references are available about flow regime on laboratory scale trickle bed columns, so we will accept that industrial regime flows can be extrapolated to laboratory scale with some restrictions.

To ensure that the system flow operated under the trickle bed region, liquid and gas phases must flow with a Reynolds number lower than 10³ [35]. Experiments set were designed to work in the upper part of the trickled flow zone (little white dots, Figure 2), although some points with highest liquid and gas flow rates were in the pulsed flow region (black squares, Figure 2). Even if some experiments were in the border line of the pulsed flow regime, the results were consistent. Because of that, all of the experiments were performed in the same series independently of the flow regime.

A TBR is a flexible solution to support hydrogen peroxide direct synthesis because it guarantees a high mass transfer coefficient between gas, liquid and solid phase. In general, it is quite difficult to understand the relation between the reactor system and the mechanism of the reaction studied, especially for the H₂O₂ direct synthesis. For that reason, it is important to study all the reactor parameters and to relate them to the catalyst activity and to the possible reaction mechanism. Only with this systematic work can new information be acquired and used for catalyst design [29]. Thus, it is necessary to monitor the reaction variables in terms of the productivity and stability of the reaction system.

The reaction conditions must be selected carefully to avoid that one reaction stage (mass transfer or kinetic control) which could limit the process. Success

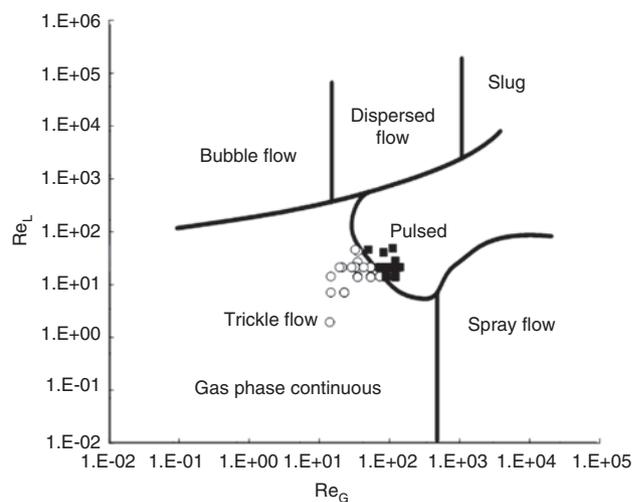


Figure 2: Trickle bed region and operational window (adapted from Ranade et al. [35]).

in hydrogen peroxide direct synthesis depends on the liquid flow rate relative to gas flow rate and the amount of catalyst: with a correct selection of them, it is possible to reduce the production of water, as already demonstrated [7, 18, 22, 29]. Liquid flow rate, gas flow rate and the catalyst amount are all coupled. Indeed, it is important to analyse them together to understand how H₂ should be fed and consumed in the reactor to minimize all the reactions that are forming water. Secondary reactions are related to the amount of hydrogen available in the liquid phase and its consumption rate [18, 37]. H₂O₂ productivity could increase with the gas flow rate (higher amount of H₂) only if the gas can be dissolved into the liquid phase (mass transfer) and further consumed (kinetics).

3.1 Influence of liquid flow rate/gas flow rate and catalyst amount

Liquid flow rate must be high enough to ensure complete and homogenous wetting of the reactor bed. Upper liquid flow rate value is limited by flow regime region because experimental conditions must be designed in order to ensure the trickle flow regime. With these limitations, 4 ml·min⁻¹ and 6 ml·min⁻¹ were selected as the operational liquid flow rates.

For 4 ml·min⁻¹ flow rate (Figure 3), the increase in the H₂O₂ production was linear for each amount of catalyst,

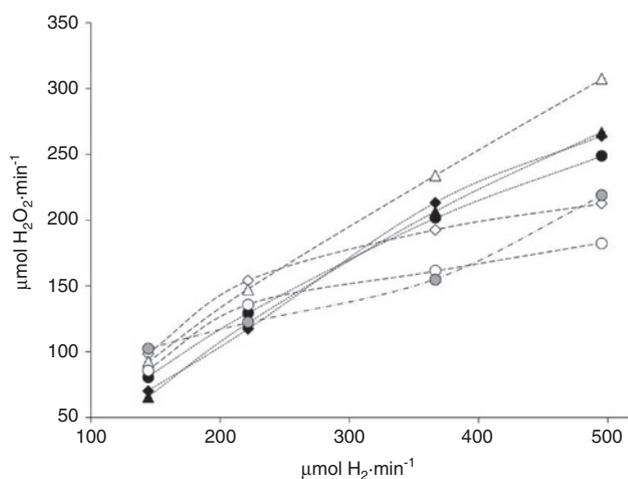


Figure 3: Influence of liquid flow rate, gas flow rate and amount of palladium on hydrogen peroxide production rate. (#1–16; 21–32)^a. 15 barg, 15°C, 5% Pd/C, [Br]=5×10⁻⁴. ● 150 mg of catalyst, 4 ml·min⁻¹; ○ 150 mg of catalyst, 6 ml·min⁻¹; ● 150 mg of catalyst, 15 ml·min⁻¹; ◆ 380 mg of catalyst, 4 ml·min⁻¹; ◇ 380 mg of catalyst, 6 ml·min⁻¹; ▲ 540 mg of catalyst, 4 ml·min⁻¹; △ 540 mg of catalyst, 6 ml·min⁻¹.
^aSee Supplementary Material.

thus indicating that hydrogen in the liquid phase (catalyst from 150 mg to 580 mg) was not limiting the reaction. However, at these catalyst loadings, the production rates were very similar indicating that the mass transfer regulated the H₂O₂ direct synthesis reaction. The hypothesis to explain this behaviour can be summarized as follows: the direct synthesis of H₂O₂ and direct formation of H₂O are the reactions that compete at the beginning, while hydrogenation and decomposition are the reactions that are only commenced after a significant amount of H₂O₂ is produced [18, 37]. Most probably, since the liquid flow rate was not very high, the catalyst consumes all the hydrogen in the first part of the reactor, thus minimizing H₂O₂ hydrogenation (since a high amount of catalyst means high activity and high velocity of H₂ conversion and consequently high rates for H₂O₂ and H₂O production when no H₂O₂ is present in the reactor). Hydrogenation for 4 ml·min⁻¹ was quite low, around 10% along the bed (Supporting Information). This means that hydrogenation was not affecting so much the reaction, but most probably the formation of water was due to the direct synthesis of water at the beginning of the catalyst bed (Supporting Information: it was observed that hydrogenation is 0 order with respect to H₂O₂ but order more than 1 with respect to H₂). For 6 ml·min⁻¹ flow rate (Figure 3), the results were different. The experiments with 540 mg of catalyst displayed a linear increase of the H₂O₂ with the H₂ content in the feed. The experiments with 380 mg and 150 mg of catalyst behaved differently; a linear increase of H₂O₂ was observed from 120 μmol·min⁻¹ up to 220 μmol·min⁻¹ of H₂ in the feed, while after 220 μmol·min⁻¹ of H₂ a nonlinear increase in H₂O₂ concentration was observed. The explanation can be quite simple: with 540 mg catalyst, the reactions that consume H₂ to form H₂O₂ and H₂O take place in the first part of the reactor and all H₂ is consumed to form H₂O₂ and H₂O. Hydrogenation was not occurring in this case or was negligible (as discussed previously about the catalyst dynamics during the reaction). The H₂O₂ formed could only decompose since H₂ was no longer present in the liquid phase (and decomposition was negligible as already explained). So, the most probable reactions to occur were only the direct formation of H₂O₂ and H₂O. With 380 mg and 150 mg of catalyst, H₂ also reacts in the second part of the reactor. In this case, a competition between H₂O₂ and H₂O production and H₂O₂ hydrogenation can be hypothesized. There is a competition between the phenomena of adsorption on the catalyst surface, and these phenomena are related to the catalyst amount, catalyst oxidation state, H₂ concentration in the liquid phase and to the gas and liquid flow rates. It is important to underline that the dynamics of the catalyst depend on the reaction conditions used.

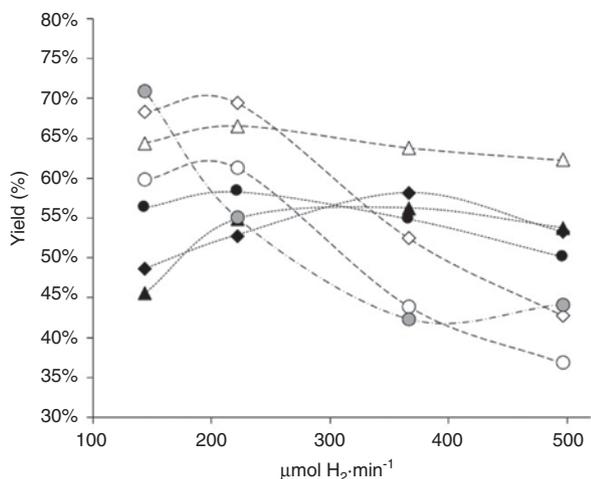


Figure 4: Influence of liquid flow rate, gas flow rate and amount of palladium on average final yield value. (#1–16; 21–32)^a. 15 barg, 15°C, 5% Pd/C, [Br]=5×10⁻⁴. ◆ 380 mg of catalyst, 4 ml·min⁻¹; ◇ 380 mg of catalyst, 6 ml·min⁻¹; ▲ 540 mg of catalyst, 4 ml·min⁻¹; △ 540 mg of catalyst, 6 ml·min⁻¹; ● 150 mg of catalyst, 4 ml·min⁻¹; ○ 150 mg of catalyst, 6 ml·min⁻¹; ◎ 150 mg of catalyst, 15 ml·min⁻¹.^aSee Supplementary Material.

The yield followed the same trend described previously. Yield (Figure 4) was quite stable for the experiments with 540 mg of catalyst, but decreased quite rapidly for other amounts of catalysts at 6 ml·min⁻¹. It seems that the reaction depends strongly on the palladium centres (active sites on the surface) and their distribution along the reactor, as well as the equilibrium of the adsorption between H₂, O₂ and H₂O₂ [11, 35, 36]. This equilibrium can be shifted with the reactor conditions to minimize the H₂O₂ hydrogenation. Moreover with proper catalyst design, the H₂O₂ production can be increased since it seems also that direct water formation only occurs on specific palladium centres of the catalyst [2, 7, 9, 38–40]. The last series of experiments performed with 150 mg of catalysts and 15 ml·min⁻¹ of liquid flow rate exhibited an interesting trend: when the hydrogen flow rate was low, the production was high in comparison. Upon a feed rate of 120 μmol·min⁻¹ of H₂ the yield was high as well, but when the H₂ feed was increased, the production rate only increased little and the yield drastically decreased. These results are in accordance with the previous observations related to the gas-liquid mass transfer and to the possibility of the hydrogen to directly form H₂O₂ and H₂O or to hydrogenate the H₂O₂ formed (these observations are based on contact time between liquid and active metal phase). Too much hydrogen is detrimental for the reaction, and what is needed is probably a multiple injection system or a system that consists of numerous consecutive reactors with small beds and a H₂/O₂ recharge between every bed.

3.2 Influence of total pressure

Mass transfer limitations between gaseous reactants (hydrogen and oxygen) and the active centres of the catalyst restrict system effectiveness and reduce productivity. Mass transfer can be enhanced in different ways. An excess of catalyst (540 mg 5% Pd/C) was used to test this hypothesis. Thus, a higher operational pressure can improve hydrogen peroxide direct synthesis by increasing gas solubility in the liquid phase as shown in Figure 5 (9.8·10⁻⁶ molH₂·molH₂O⁻¹ at 28 barg and 15°C; 1.3·10⁻⁶ molH₂·molH₂O⁻¹ at 5 barg and 15°C). Greater amounts of gas dissolved in the liquid phase means higher hydrogen peroxide productivity.

A comparison between experiments 16 and 35 (Supplemental Table 4 in the supplemental material) showed how the volumetric flow rate plays a very important role. Hydrogen reacted to first produce H₂O₂ and H₂O. If much H₂ was present in the bottom part of the reactor, competition between hydrogenation and the H₂O₂ formation was present, thus favouring the hydrogenation reaction. The pressure in experiments 13 and 16 (Supplemental Table 4 in the supplemental material) was equal and the yield was comparable, even if the hydrogen molar flow rate at experiment 13 was almost 3.5 times lower. The difference in these experiments is the H₂ concentration at the inlet. Probably the consumption rate of H₂ was similar and the main reactions involved were only the direct synthesis of H₂O₂ and H₂O. Analysing experiments 35 and 55, one can state that the lower liquid flow rate resulted in a high yield, while a higher liquid flow rate resulted in pronounced hydrogenation, as observed before. Experiment

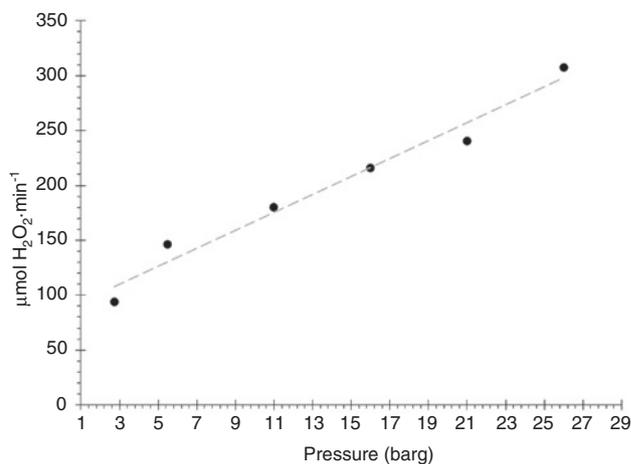


Figure 5: Influence of reactor pressure on final average hydrogen peroxide molar flow rate. (#33–37)^a. 15°C, 540 mg of catalyst 5% Pd/C, 6 ml·min⁻¹, 469 μmol H₂·min⁻¹, [Br]=5×10⁻⁴.

^aSee Supplementary Material.

20 demonstrated again how mass transfer and concentration of reagents and catalyst play an important role on the reaction mechanism and how the reaction network of the H₂O₂ direct synthesis should be managed. A comparison from these experiments can demonstrate that a high pressure does not guarantee a higher productivity or yield, but it has to be fine-tuned experimentally to achieve excellent results. The linear tendency indicated that all of the reactions are influenced in the same way by the pressure.

3.3 Influence of temperature

Experiments in series (38–42, Supplemental Table 1 in the supplemental material) were carried out with a high amount of catalyst (540 mg of 5% Pd/C), high liquid flow rate (6 ml·min⁻¹) and high hydrogen molar flow rate (496 μmol H₂·min⁻¹) to ensure high mass transfer rates between gas and liquid phases. Consequently, a volcano shape trend was observed. To explain this behaviour, it is appropriate to consider the activity of the catalyst. Lower temperatures retard the H₂ consumption. This can be seen clearly when observing the hydrogenation reaction. Nevertheless, the temperature and the productivity rates reflect different effects: H₂ consumption rate, H₂O₂ hydrogenation, synthesis of H₂O. An optimum of the above mentioned effects can be found around 20–40°C (Figure 6).

Even if selecting the most appropriate operational conditions, the results do not show a linear tendency or a clear optimum value under these conditions. Within the temperature interval analysed, three different sections

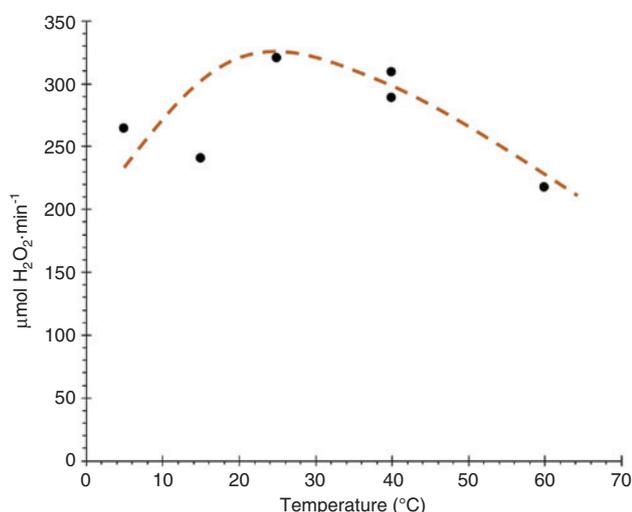


Figure 6: Reaction temperature vs. hydrogen peroxide production rate. (#33, 38–42)^a. 20 barg, 540 mg of catalyst 5% Pd/C, 6 ml·min⁻¹, 469 μmol H₂O₂·min⁻¹, [Br]=5×10⁻⁴.

^aSee Supplementary Material.

can be seen. At low (5°C and 15°C) and high (60°C) temperatures, hydrogen peroxide productivity reflected moderate values between 218 μmol H₂O₂·min⁻¹ and 264 μmol H₂O₂·min⁻¹, probably due to low reaction rates and slow kinetics, as well as higher hydrogenation rates when high temperatures were applied. Highest productivity values (309 μmol H₂O₂·min⁻¹ and 320 μmol H₂O₂·min⁻¹) were obtained at intermediate temperatures (25°C and 40°C). Similar tendencies were obtained in terms of yield and turnover frequency values. Over 25°C, the direct water formation and the hydrogenation prevails due also to the higher solubility of hydrogen compared to the other gases.

3.4 Influence of bromide concentration

Liu and Lunsford [38, 39] proposed that H⁺ reacts with an active form of oxygen to produce H₂O₂ and acts over the electronic state of active metal to facilitate H₂O₂ formation. Protons could also act as boosters enhancing the adsorption of halide ions by lowering the pH below the isoelectric point [26, 27]. Dissociative adsorption of O₂ and H₂O₂ as well as cleavage of the bond O-O may take place over the more energetic active centres (edge, corner or defect) of the catalyst. Halide anions could block the most active sites and thus counter-effect decomposition or act as an electron scavengers and inhibit radical-type decomposition reactions.

Deguchi and Iwamoto [41, 42] proposed a reaction mechanism based on kinetic analysis. Based on this analysis, it was concluded that H⁺ accelerated Br adsorption and it was responsible for adsorption and desorption of some reaction intermediates. Irrespective of the bromide effect, Deguchi and Iwamoto reached similar conclusions proposing that bromide is adsorbed on the most energetic active sites and thus reduces the decomposition and hydrogenation probability.

It is still unclear what are truly the dynamic effects in terms of bromide, on the H₂O₂ direct synthesis. Figure 8 might give some insight into this mystery.

Sodium bromide and phosphoric acid were chosen as promoters. For this purpose, three experiments carried out at three sodium bromide concentrations were selected (1×10⁻³ M; 5×10⁻⁴ M; 2.5×10⁻⁴ M). Acid concentration was kept constant (pH equal to 2). Unlike during the remaining experiments, hydrogen concentration was measured every 15 min from the very beginning (without waiting until the steady state condition prevails). This was the first time the H₂O₂ production was measured during the start up until the steady state with different amounts of bromide (Figure 7). The experiments performed without NaBr and H₃PO₄

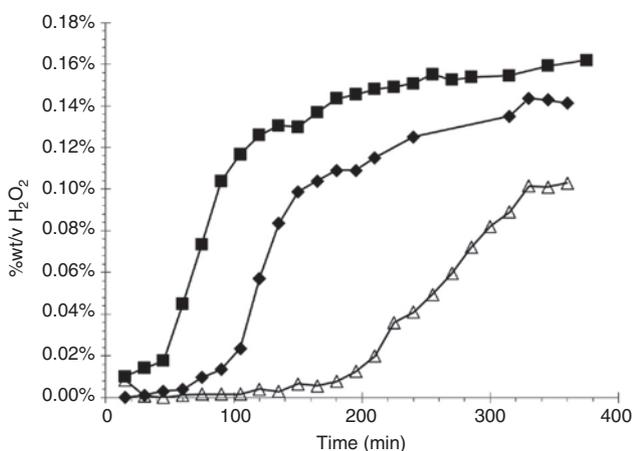


Figure 7: Evolution of hydrogen peroxide during the course of reaction and the influence of bromide concentration. (#54–56)^a. 10 barg, 15°C, 540 mg of catalyst 5% Pd/C, 2 ml·min⁻¹, ■ [Br]=1×10⁻³ M, 141 μmol H₂·min⁻¹, ◆ [Br]=5×10⁻⁴ M, 141 μmol H₂·min⁻¹, △ [Br]=2.5×10⁻⁴ M, 141 μmol H₂·min⁻¹.
^aSee Supplementary Material.

resulted in complete conversion of H₂ but no observed H₂O₂. It is interesting to see the non-steady state curves: during the first part, H₂O₂ increases slowly and then, depending on the NaBr concentration, H₂O₂ production sharply increases to reach a steady state (Figure 7). Previously, it was seen that as a result of NaBr addition, the shape and the dispersion of the nanoparticles of the catalyst changed (the dimension of the nanoparticles size increased) [18]. Most probably, there is a phenomenon of adsorption/desorption of the Br to block the sites responsible for H₂O formation. Also, reconstruction of the nanocluster was probably needed before active sites for H₂O₂ formation emerge [11, 34]. These phenomena are correlated with the NaBr quantity. The more NaBr there is in the solution, the faster is the reconstruction of nanoparticles/site blocking of the catalyst to reach steady state conditions (i.e. stable concentration of the H₂O₂). Moreover, more NaBr boosts higher maximum H₂O₂ concentrations reached. The liquid flow rate and the gas flow rates were fixed, and the only variable was the NaBr concentration. An analysis of the data suggests the following conclusions: Br blocks the sites for both H₂O₂ and H₂O formation, but the effect of the bromide is higher on the sites for direct formation of water. 1) The quantity of the Br not only affects the quantity of the sites, but also the quality of the sites that are blocked. Indeed, doubling the concentration of Br does not mean doubled final concentration of H₂O₂. Consequently, the amount of Br not only influences the sites responsible for H₂O formation, but also the ones for the H₂O₂ direct synthesis and for H₂O₂ hydrogenation and direct water formation [11, 18]. It seems that higher bromide concentrations strongly

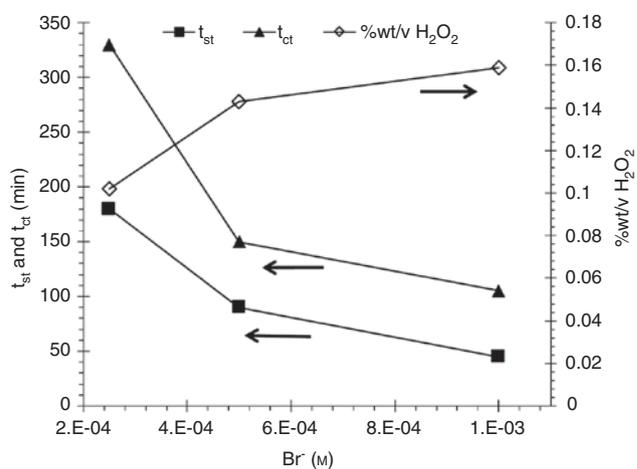


Figure 8: The bromide concentration effect. (#54–56)^a. 10 barg, 15°C, 540 mg of catalyst 5% Pd/C, 2 ml·min⁻¹. t_{st}: reaction starting time, t_{ct}: reaction steady state.
^aSee Supplementary Material.

influence H₂O₂ hydrogenation reaction (Figures 7 and 8). 2) The time to reach the steady state for H₂O₂ production varied when different concentrations of NaBr were used. Thus, reconstruction of the metal nanoclusters and adjustments in adsorption/desorption equilibrium phenomena of the Br on the Pd surface are likely affected (Pd surface types are also related to the sites that are available for the different reactions) (Figures 7 and 8). Moreover, Figure 7 shows an interesting trend. The trend looks like the catalyst light off during catalytic combustion experiments. From the results, it seems that the procedure of site blocking by NaBr occurs in different steps. First, Pd leaching is enhanced by NaBr at the beginning, with low formation of H₂O₂ and its hydrogenation. This fact led to the reconstruction of the nanocluster and of the Pd surface. Then, the sites for the H₂O and H₂O₂ formation are blocked by NaBr. In this way the results (and the shape of the slopes) in Figure 7 can be explained. Depending on the NaBr, the unwanted reactions are suppressed, and this suppression is related to the amount of NaBr. The NaBr is not selective in the site blocking, otherwise reducing the amount of it would have resulted in a more enhanced effect on the direction of water formation suppression of H₂O₂ formation suppression.

The hypotheses described above can be verified against experimental data.

4 Conclusions

As a summary we can conclude that H₂O₂ direct synthesis is a challenging reaction and to understand the real

mechanism, different parameters have to be studied. Despite the work efforts towards tuning the reaction for maximum H₂O₂ concentration, it was more important to try to understand how the reaction conditions affect the mechanism of the H₂O₂ direct synthesis and how to use this information for reactor design. Fast hydrogen consumption to produce the H₂O₂ was clearly seen as beneficial when high mass transfer limitations prevailed (6 ml·min⁻¹) or with a high amount of catalyst present (540 mg of 5% Pd/C catalyst). By contrast, when experimental conditions and catalyst distribution along the column did not allow for fast consumption of hydrogen, a decrease in the yield could be expected because of H₂O₂ hydrogenation. This was observed when a high-loaded Pd catalyst was applied. Indeed, if there is a high distribution of the Pd active sites along the catalytic bed, the hydrogenation reaction is also highly enhanced. A volcano shaped temperature effect was revealed since both H₂O₂ formation and its hydrogenation rates were increased with temperature. However, formation of water is affected more compared to the direct synthesis when temperature is increased. To avoid hydrogenation, slow hydrogen consumption is needed along the catalytic bed. To do this, it will be important in the future to work with new reactor concepts for H₂O₂ direct synthesis: multiple injection system, a system that consists in numerous consecutive reactors or recirculation with a low amount of catalyst loaded in the reactor.

The effect of the Br on the metal cluster is challenging to quantify, but some indications can be drawn. The Br indistinctly affects the sites for H₂O₂ direct synthesis and water formation. Moreover, it seems that not only the phenomenon of adsorption/desorption of Br on the Pd surface but something more complicated occurs.

A new mechanism and effect of NaBr in the direct synthesis was proposed: NaBr site blocking as a process that works with different steps: 1) Pd leaching and surface reconstruction; 2) hydrogenation/water formation sites blocking; 3) H₂O₂ site blocking. All the steps are highly affected by the NaBr amount present in the reaction medium. Modifying the NaBr amount coupled with the tuning of the gas flow rates will help in identifying the most promising conditions to avoid water production.

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