BRIDGING THE GAP BETWEEN CHEMISTRY AND CHEMICAL REACTION ENGINEERING IN THE DIRECT SYNTHESIS OF HYDROGEN PEROXIDE

Tapio Salmi[*], Nicola Gemo, and Pierdomenico Biasi
Department of Chemical Engineering, Åbo Akademi University, Biskopsgatan 8,
ÅBO-TURKU, FI-20500, Finland

Abstract

Hydrogen peroxide direct synthesis was experimentally studied in three different reactors: batch, semibatch and trickle bed reactor (TBR) using a new promising catalyst based on Pd/K2621. Excellent results were obtained from experimental point of view, achieving high H_2O_2 selectivities, around 90% at short contact time in batch, 60% in semibatch and 70% in TBR. The simplest rate equations compatible with the acknowledged reaction network were included in reactor models, which accounts for mass transfer resistances between gas and liquid and bulk of the liquid-catalyst surface. The corresponding Arrhenius parameters were estimated from direct synthesis experiments for all the reactions and reactors. The models describe how the reaction rates change between batch, semibatch and trickle bed reactor (TBR) reactor.

Keywords

H_2O_2 direct synthesis, kinetic study, partial reaction orders

Introduction

The need to have an alternative to the auto-oxidation (AO) process is strong enough to attract a lot of attention both from academia and industry. The industry of the new century needs to reduce investment costs, to delocalize the production and to have flexible solutions with low waste management. Due to its potential, the H_2O_2 direct synthesis (DS) is the reaction that will help to develop the new industry concept (Garcia Serna et al. 2014). Unfortunately, due to the lack of maturity in this research field, the commercialization of the process suffers of some lacks. The above mentioned reasons are the driving forces that still make the DS a hot topic in the scientific community (Scheme 1). Up to now the research in the direct synthesis is focused mostly on the catalyst development, but in the recent years the investigation on the process is gaining attention and importance (Centi et al. 2009). Only recently, publications demonstrated the beneficial effect of studying the reaction from a chemical reaction engineering point of view (Garcia Serna et al. 2015).
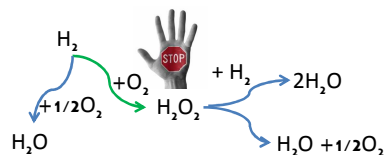
Scheme 1. Reactions involved in the DS

For the above mentioned reasons it was decided to combine the two approaches and to try to bridge the chemistry with the chemical reaction engineering. To do so, it was decided to study a novel promising catalyst

---

[*] tapio.salmi@abo.fi

(Gemo et al. 2015) with three different reactors: batch, semibatch and a trickle bed reactor (TBR).

With this approach the reaction was studied from the chemistry level to the chemical reaction engineering level, answering some of the still open issue in the DS.

Results and Discussion

In order to quantitatively compare the experimental results, the kinetic parameters of the catalyst were regressed using the experimental data in the three reactors. The calculated activation energies and pre-exponential factors of all the reactions involved (Scheme 1) are reported in Table 1.

Table 1. Activation energy and pre-exponential factors regressed in the batch, semibatch and continuous experiments.

	Batch		Semibatch		TBR	
	Ea kJ/mol	A	Ea kJ/mol	A	Ea kJ/mol	A
ds	42.6	1.47E+09	67.0	8.90E+21	6.9	3.18e+17
wf	92.3	4.38E+23	133.8	1.15E+14	8.0	5.52e+15
d	30.1	1.47E+09	58.9	1.09E+20	5.1	4.66e+3
h	53.2	1.38E+19	29.8	7.07E+02	7.3	3.87e+15

The rate of each reaction was also calculated. The results are shown in Figure 1 as ratios between the rate of the undesired reactions (water formation (R_{wf}), hydrogenation (R_h) and disproportionation (R_d)) and the DS reaction rate (R_{ds}), so to mark the favored undesired reaction.
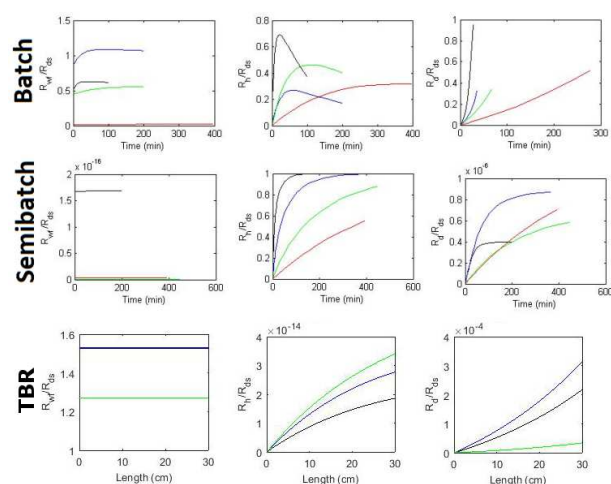

Figure 1. Ratios between water formation, hydrogenation, disproportionation and direct synthesis reaction rates in batch, semibatch and TBR experiments. ■, -10 °C; ■, 2 °C; ■, 15 °C; ■, 30 °C.

In the batch reactor the water formation compete with the direct synthesis reaction (Figure 1); however, the ratio R_{wf}/R_{ds} is larger than 1 only for the highest temperature, i.e. the water formation reaction prevails over the direct synthesis only for high temperature; at the same time, also the hydrogenation and

decomposition reactions are significant, although both the R_h/R_{ds} and R_d/R_{ds} ratios had values lower than 1. The direct synthesis activation energy is confirmed lower than that of the direct water formation (Table 1). In the semibatch, the most important reaction competing with the direct synthesis was the hydrogenation, although R_h/R_{ds} values were always lower than 1 (Figure 1). The activation energy of the water formation was higher than that of the direct synthesis, as noticed in the batch reactor (**Error! Reference source not found.**). However, the main difference between the batch and semibatch reactor is as follows: in the batch apparatus all the undesired reactions were competing with the direct synthesis, whereas in the semibatch only hydrogenation had a significant effect. TBR results showed how the hydrogenation and decomposition reaction rate are much slower than that of the direct synthesis reaction (R_h/R_{ds} and R_d/R_{ds} values much lower than 1). Moreover, the activation energy values of all the reaction in TBR was very low (< 10 kJ/mol). This means that the temperature had little effect on the reaction rates in the TBR (the opposite happens in batch and semibatch), suggesting that the experiments were carried out in the mass transfer regime.

Conclusions

Important guidelines are gained to operate in batch, semibatch and TBR to enhance the H_2O_2 production and to suppress the other reactions. To avoid the H_2O formation in a continuous reactor, short contact times are needed coupled probably with a gas-liquid recirculation, this will help to enhance the H_2O_2 production avoiding the water formation. The environment should be kept always with a high concentration of hydrogen in the liquid phase and thus favoring the H_2O_2 production. These new findings will help to design new catalysts and to engineer the reaction by maximizing the performance. To conclude, the catalyst design should be made according to the features of the reactor and not only looking at the catalyst itself. Understanding of the reaction path and progress with the three reactors helps in identifying the strategies to improve both the reaction conditions and the catalyst design.

References

Centi, G., Perathoner, S., Abate, S. (2009) Direct synthesis of hydrogen peroxide: recent advances. *Modern Heterogeneous Oxidation Catalysis, Wiley-VCH, 253.*

Garcia-Serna, J., Moreno, T., Biasi, P., Cocero, M.J., Mikkola J.P., Salmi, T.O. (2014) Engineering in direct synthesis of hydrogen peroxide: targets, reactors and guidelines for operational conditions. *Green Chem., 16, 2320.*

Gemo, N., Sterchele, S., Biasi, P., Centomo, P., Canu, P., Zecca, M., Shchukarev, A., Kordas, K., Salmi T.O., Mikkola, J.P. (2015) The influence of catalyst amount and Pd loading on the H_2O_2 synthesis from hydrogen and oxygen. *Catal. Sci. Technol., 5, 3545.*