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# Development of a monolith-based process for $H_2O_2$ production: from idea to large-scale implementation

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## Abstract

Akzo Nobel, Eka Chemicals, produces hydrogen peroxide in a large scale using the anthraquinone (AQ) autooxidation process. The key step is the highly selective liquid-phase hydrogenation of the AQs to their corresponding hydroquinones. For this step, a unique hydrogenation technology employing a monolithic catalyst has been developed and implemented.

The present contribution outlines the development of this technology from the initial idea to implementation in industrial scale. Examples taken from Ekas patents in this area are used for illustrative purposes.

*Keywords:* Monolithic catalyst; Liquid-phase hydrogenation; Hydrogen peroxide; Scale-up

## 1. Introduction

Although $H_2O_2$ can be produced in many ways, the by far dominating process is the anthraquinone (AQ) autooxidation process (see Fig. 1). A mixture of AQ derivatives is dissolved in organic solvents to form the working solution, which is cycled between three main steps:

1. a hydrogenator where AQ is hydrogenated catalytically to the corresponding hydroquinone ($AQH_2$);
2. an oxidizer where oxygen/air reacts with the $AQH_2$ to form $H_2O_2$ and the original AQ;
3. an extraction step where water is used to remove the $H_2O_2$ from the working solution.

A variety of AQs can be used and among those commonly used, we find 2-alkyl-substituted ones, e.g. 2-ethyl AQ. Further details of this process can be found in [1,2]. It is worth noticing that a very high, well above 99%, overall selectivity is required.

The hydrogenation step requires a catalyst. Initially, Raney nickel was used, but today most producers use palladium-based catalysts. Hydrogenation technologies used for this process include fixed-bed reactors using a supported Pd-catalyst as well as slurry technologies using either supported Pd-catalyst or unsupported Pd-black. Recently, the use of various forms of structured reactors has been reported as well (see [1,3,4] and references therein).

Monolithic catalysts were developed to meet the requirements for exhaust gas cleaning. The monolith combines a large geometrical surface area with low pressure drop and a high degree of uniformity which makes it suitable for a process characterized by high flowrates and a need for high selectivity. The idea of using a monolith for the AQ hydrogenation was put

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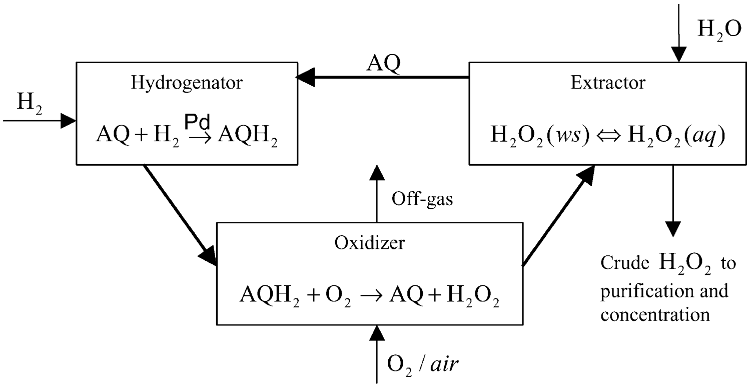

Fig. 1. The main steps of the AQ autooxidation process. The working solution is cycled between a catalytic hydrogenation, non-catalytic oxidation and an extraction step.

forward by researchers at the Chalmers University of Technology, Göteborg and picked up by Eka Chemicals. Development starts in the early 1980s and the first large-scale reactor was brought on stream a decade later. Today the new type of reactor is used in plants with a total annual capacity of approximately 200 kt. The aim of the present paper is to give an idea of what was involved in this development.

## 2. Development of a monolith technology

We may distinguish two major lines of development: the development of a monolithic catalyst and the development of an appropriate reactor technology. Needless to say these are not independent.

### 2.1. Catalyst support

There are a number of requirements affecting the choice of support, some of which are independent of the shape of the catalyst. An example is the chemical compatibility with the process chemicals. Among useful support materials reported in literature we find carbon, $Al_2O_3$, $SiO_2$, where the latter was chosen.

Next, it must be possible to shape it as a monolith and it must have sufficient mechanical strength in order to allow large structures which are capable of carrying the load from the catalyst, the liquid held-up and possible pressure drop. In catalysts for gas treatment at high temperature, this is typically done by a combination of a backbone providing strength (metal or ceramics) and a porous washcoat providing the surface enlargement needed for the catalysis. In this case, the process is operated under relatively mild conditions (few bars, 40–70°C) and it turned out to be possible to use a simpler approach in which a reinforced amorphous silica is used throughout the wall [5]. Such monoliths were not available on the market and a method for making them became an important part of the initial development.

Once we have the monolithic support, we need to deposit the catalytically active phase, i.e. the Pd, on it. This is complicated by the fact that a large piece of catalyst has to be handled. One useful method for preparing large pieces of catalysts is outlined below:

The procedure is called electroless deposition and involves chemical reduction of a Pd-containing solution. It actually consists of three steps where the first two can be viewed as a preconditioning of the support. A more-detailed account can be found in [6].

1. *Sensitizing*:
    1.1. Contacting the porous silica support with an aqueous acidic $SnCl_2$ solution for 2 min.
    1.2. Washing with water.
2. *Activation*:
    2.1. Immersing the sensitized support in an acidic aqueous $PdCl_2$ solution for 2 min.
3. *Electroless deposition*:
    3.1. Immersing the activated support in an aqueous mixture of $NH_3$, $NH_4Cl$ and $PdCl_2$.

3.2. Slow addition of an aqueous solution of $NaH_2PO_2$.
3.3. Washing in acidic water solution and then drying at 50°C overnight.

### 2.2. Catalyst testing

In preparation of the support as well as in the metal deposition, there are a fair number of preparation parameters that influence the properties of the final catalyst, such as pore volume and size, the total metal loading, dispersion and distribution of metal, both locally (within the porous wall) and globally (between various parts of a larger piece). In order to optimize these parameters, it is necessary to test the catalyst. Although some aspects of preparation can be tested using ground catalyst, testing of larger pieces of monoliths remains essential. This necessitated the development of bench and pilot scale test reactors. A bench scale batch reactor is sufficient for testing the activity of the catalyst as a first test. This scale is also appropriate for deactivation tests. A larger scale is needed in order to verify the function from a hydrodynamic point of view.

A complicating factor here is actually the excellent selectivity needed and achieved. It is so close to unity that it is difficult to measure accurately in a single pass. In practice, a continuous pilot plant including the whole cycle of the autooxidation process is needed.

The two main aspects of aging that need to be checked is the loss of catalytic activity and the possible loss of mechanical strength. As it turns out, the mechanical strength can be maintained for a large number of years. The loss of activity is a slow process and can be attributed to fouling.

### 2.3. Catalyst regeneration

A procedure involving washing with an acidic solution has been developed and shown to restore a significant part of the activity. The procedure consists of the following steps:

1. treatment with a non-polar organic liquid, e.g. Shellsol$^{TM}$, for 48 h;
2. treatment with acetone (1 h) and drying (2 h), optional;
3. two successive treatments with a mineral acid for 3 h;
4. rinsing in de-ionized water.

The effect of treatment with different acids is illustrated in Fig. 2. More details on this procedure can be found in [7].

### 2.4. Reaction engineering

The second large line of development focuses on the reaction engineering aspects, by which we include the design of the reactor and the mode of operation.

At an early stage of the development, a comparative study was made between a slurry reactor, a fixed-bed (trickle-bed) reactor and the monolith reactor [5]. The tests were carried out using a loop reactor illustrated in Fig. 3. This pilot reactor was part of a pilot system including all the main stages of the autooxidation process. It could be fitted with either a monolithic

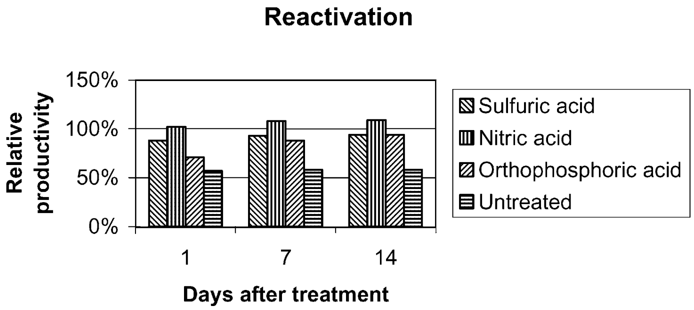

Fig. 2. The relative productivity of regenerated catalysts depending on the mineral acid used. Relative productivity is defined as the productivity (in $kg(H_2O_2)/m^3\,h$) of the catalyst relative to a virgin catalyst used for the same number of days. The optional acetone treatment was applied only in the case of orthophosphoric acid (from [7]).

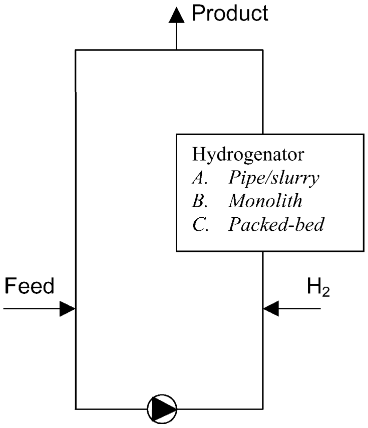

Fig. 3. Loop reactor set-up used for comparing different hydrogenators (from [5]).

catalyst or with a fixed-bed catalyst. By using an empty pipe instead, it could be operated as a slurry reactor. The results are summarized in Table 1. Noteworthy are the high selectivity (low AQ losses) and the high rates obtained even after a long time on stream.

### 2.5. Catalyst handling

The monolith pieces are large, with dimensions in the order of meters, which makes handling relatively easy. The large pieces are mounted in frames, which turns out to be very practical when loading/unloading a reactor, this can be done quickly since only a few large assemblies need to be handled. A second advantage is that this opens up the possibility to keep track of the individual pieces of catalyst.

### 2.6. Hydrodynamics

The problem of obtaining hydrodynamically good conditions is critical to all gas/liquid/solid reactors and the most important challenges are listed below.

1. create good mass transfer from both the gas and the liquid phases to the solid catalyst;
2. avoid the formation of local hot spots;
3. generate a uniform flow;
4. allow an up-scalable flow;
5. permit removal of the heat of reaction.

A finding, in the initial testing using a small diameter monolith and fairly high flow rates, was that the direction of flow made little or no difference and up-flow was chosen. When moving to larger scale, it became difficult to obtain good distribution over the whole reactor cross-section. The gas was introduced as small bubbles through a poral filter and as they rose through the submersed bed, channeling occurred leading to a low utilization of the catalyst. It was then found that down-flow offered several advantages:

- Uniform distribution of the liquid could be achieved.

Table 1
Comparison of monolithic, slurry and packed-bed reactors[a]

| Type | Slurry | Monolith | Packed bed |
|---|---|---|---|
| Catalyst type | Pd-black | Pd on porous silica gel applied to a glass-fiber matrix | 0.3 wt.% Pd on alumina, 2 mm spherical |
| Catalyst volume ($dm^3$) | Very small | 1 | 0.5 |
| Bed diameter (mm) | – | 80 | 80 |
| Flow direction | – | Mostly upwards | Downwards |
| Circulation rate (l/min) | | Up to 300 | 30 |
| Duration (h) | 1000 | 1250 | 1000 |
| AQ conversion (%) | 45 | ∼60 | |
| *Productivity* | | | |
| $g(H_2O_2)/g(Pd)$ (h) | 16 | 80 (start) | 105 (start) |
| $g(H_2O_2)/g(cat)$ (h) | 16 | 533 | 314 |
| | | 97% (after 1250 h) | 85% (after 1000 h) |
| *Selectivity* | | | |
| mmol(AQ-lost)/mol($H_2O_2$) | 0.18 | 0.10 | 0.25 |

[a] Pressure was 2 bar and temperature 55°C (from [5]).

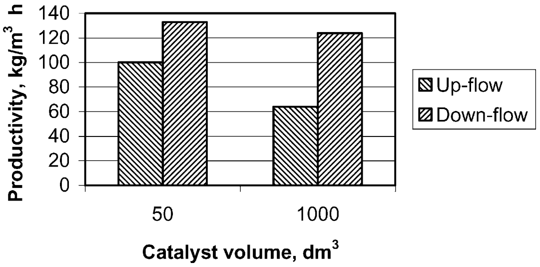

Fig. 4. Comparison of flow directions for two sizes of pilot reactors. An AQ-containing working solution was hydrogenated at 52°C and a (mean) pressure of 400 kPa. Liquid flow rate was 0.16 $m^3/m^2$ s and the test was run for 10 days (50 $dm^3$ catalyst) or 30 days (1000 $dm^3$ catalyst) (from [8]).

- Taylor flow was obtained over a wide range of flowrates.
- Essentially constant pressure could be established, since flow is gravity driven, this allows spontaneous internal or external gas recirculation provided that there is an open connection between the top and bottom of the reactor.

A comparison between up-flow and down-flow mode of operation was done and is illustrated in Fig. 4. We see that the productivity is higher in down-flow mode. It is also worth noting that the scale effect is much larger in up-flow mode.

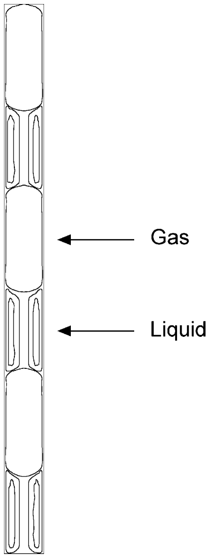

Fig. 5. Taylor (or plug) flow of gas and liquid through a narrow channel.

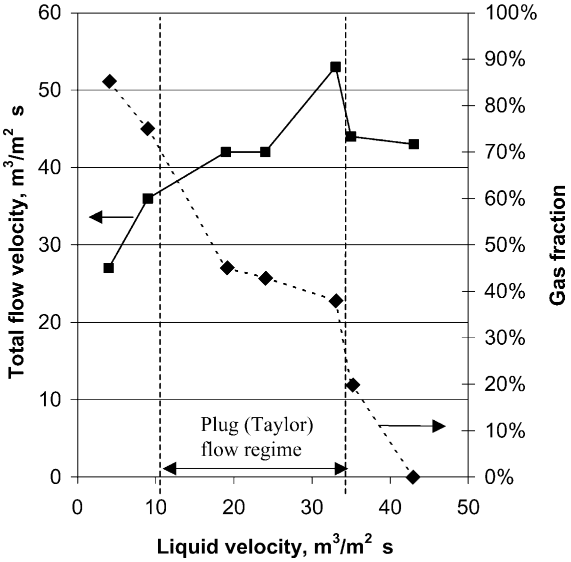

Fig. 6. Flow of AQ-containing working solution through a glass tube ($d$ = 1.5 mm, $L$ = 200 mm) coated internally with silica (from [8]).

The desired flow pattern is Taylor flow (see Fig. 5) which provides excellent mass transfer due to the large gas–liquid contact area, the short diffusion distance to the channel wall and the internal circulation induced in the liquid plug. In order to determine the flow rates under which this flow pattern is realized, a simple test was done in a glass tube ($d$ = 1.5 mm, $L$ = 200 mm) coated internally with silica [8]. The results are shown in Fig. 6. We note that the falling rate was ca 0.4 $m^3/m^2$ s and that the flow became unstable at flow rates below 0.1 $m^3/m^2$ s.

Having established flow direction and flow rate, we still need a way of distributing the liquid over the whole cross-section. It turned out that a perforated plate was adequate for this as is discussed in [9].

## 3. Conclusions

The concept of using a monolithic catalyst on a large scale is a successful one. AQs dissolved in an ordinary organic solvent can be hydrogenated with extremely high selectivity at a high productivity. A chemically and mechanically stable monolithic catalyst can be produced in large quantities and handled in a very simple way. Next to the mechanical design of a hydrogenation reactor, it is possible to find a window of operating conditions that give steady and satisfactory operation over prolonged periods of time.

It should also be realized that the road from idea to large-scale implementation is a long one. Next to the process development itself, it is often necessary to develop the tools needed for the development. Prime examples are the lab and pilot reactors used for testing the catalyst and the tools for manufacturing the catalyst.

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