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Characterization of the performance of an industrial monolith reactor by accurate mapping of temperature differences

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Abstract

The performance of a liquid-phase hydrogenation carried out in a monolithic reactor on an industrial scale has been studied by measuring temperature differences accurately. The process studied is the hydrogenator in the autoxidation process for large-scale production of hydrogen peroxide by Eka Chemicals, Akzo Nobel.

Temperature differences are primarily caused by the exothermic reaction and can be used to measure variations in local reaction rates. Non-uniformities in liquid flow distribution can also be detected. One important finding was the existence of multiple steady states that can be attributed to the stop/startup procedure.

Keywords: Liquid-phase hydrogenation; Exothermic reaction; Monolith

1. Introduction

There are many examples of liquid-phase hydrogenations for which the use of a monolithic catalyst has been considered. The industrially most important application today is the hydrogenation of anthraquinones dissolved in a mixture of organic solvents. This constitutes a main step in the autoxidation process for hydrogen peroxide manufacture and is practiced by Eka Chemicals on the scale of 200 ktpy [1]. For a general description of the autoxidation process see, e.g. [2]. For some examples of other applications for which monoliths have been considered see [3–7]. An important factor influencing the performance of any multiphase reactor is the usually complex hydrodynamics. A number of studies has been devoted to the hydrodynamics and scale-up of monoliths for gas/liquid applications [8–12].

The objective of the present contribution is to demonstrate how the important aspects of the performance of an industrial monolith reactor can be characterized in surprising detail by measuring temperature differences in several places with high accuracy.

2. Experimental methods

The measurements were carried out in a large industrial monolith reactor used for hydrogenation of a working solution in the hydrogen peroxide process (see Fig. 1). The working solution consists of anthraquinones and anthraquinone derivatives dissolved in a mixture of organic solvents. The reactor consists of a number of catalyst assemblies stacked on top of each other with some intermediate spacing. The liquid is fed at the top and distributed over the cross-section and flows downwards driven by gravity only. The flow of liquid also drives the flow of gas through the monolith beds. As the pressure is essentially constant in the reactor unreacted hydrogen is free to recirculate internally. The liquid is recirculated externally and the temperature is controlled by cooling the loop flow.

Temperature is measured in various positions in the reactor. We will here consider the following locations indicated in Fig. 1:

- Working solution feed at the top of the reactor.
- Each quadrant below the three topmost monolith assemblies.

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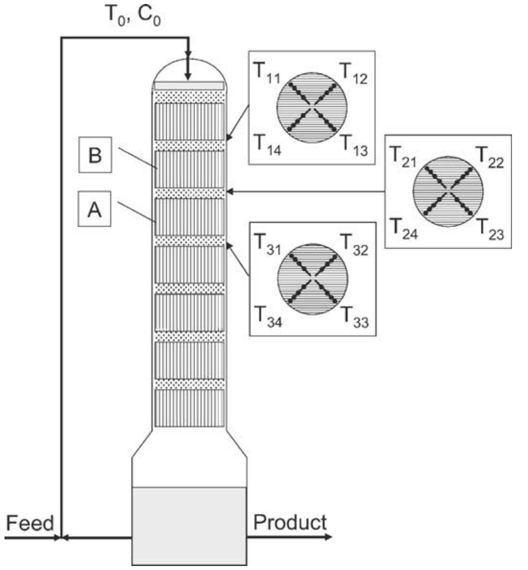

Fig. 1. Schematic view of the hydrogenator and the location of the temperature sensors. Each sensor is hardwired to produce a signal that represents an average of four different measuring points unevenly distributed along the radius as illustrated by the small black circles.

The temperature measurement below each quadrant actually represents an average of four readings in slightly different positions. Four PT100 elements have been connected in a series/parallel way in order to produce an averaged signal. Furthermore, the sensors were located non-uniformly in the radial direction to better reflect that most of the area available to flow is located far from the center according to:

$$\frac{r_i}{R} = \sqrt{\frac{1+2(i-1)}{2N}}, \quad i = 1, 2, \ldots, N. \tag{1}$$

Here, r_i is the radial position of sensor i, R the reactor radius and N is the number of sensors, here $N = 4$. At startup the reactor was operated with an inert gas, nitrogen. Under such conditions no reaction takes place and it can be assumed that the liquid temperature is the same in all positions. At this point the signals were calibrated to be internally consistent, i.e. show the same value. As we will see later, repeating this non-reactive mode of operation months later demonstrated that the internal consistency of the temperature readings was not lost.

The signals were connected to the plant data acquisition system and typically logged every 10 s for a couple of years.

The hydrogenation reaction is exothermic and the reactor is, for practical purposes, adiabatic. Hence, we may with good accuracy assume a simple proportionality between change in temperature and conversion, x, over the reactor:

$$T - T_0 = \frac{-\Delta H}{\rho c_{\mathrm{P}}} C_0 \frac{C_0 - C}{C_0} = k_1 x \tag{2}$$

Here, T is the local temperature, T_0 the inlet temperature at the top, ΔH the heat of reaction, ρ density, c_{p} the liquid heat capacity, C_0 and C the reactant concentration at the top and locally and k_1 is the adiabatic temperature rise corresponding to 100% conversion (all in SI units). By mapping temperature differences we can indirectly obtain a mapping of conversion at various positions. There are three major advantages of measuring temperature compared to withdrawing samples for chemical analysis:

- The accuracy of the conversion determination by temperature difference is an order of magnitude better than by chemical analysis. A monolith is typically operated at very high superficial liquid velocities, in the order of 10 cm/s, and the change in conversion is thus small.
- The amount of data generated. Accurate continuous chemical analysis in numerous places in situ is not feasible.
- Cost efficiency. Highly accurate temperature measurements are standard and can be done at relatively low cost.

In the present paper we will address two issues:

- How can we compare the performance of two different catalysts?
- How can we characterize liquid flow rate in terms of globally uniform distribution?

Catalysts may differ for several reasons. Here, we will consider the case of two catalysts prepared in somewhat different ways. We will also consider the effect of aging. Furthermore, if the catalysts are different then their relative performance may depend on the operating conditions. In this case, the comparison will be between two new catalysts denoted A and B that are placed in positions 3 and 2 from the top, respectively. The operating conditions for these will be very similar as most parameters are essentially the same, e.g. liquid flow rate, heat capacity and heat of reaction, catalyst volume. Two important factors, temperature and conversion differ slightly. Here, catalyst A will operate at a slightly higher temperature, which will contribute to an increased productivity, but at the same time it operates at a slightly higher conversion, which has a negative influence on the reaction rate. By experience we know that these two effects approximately cancel each other. Hence, we can with good accuracy determine the relative productivity, Π, by considering the ratio of the temperature increases:

$$\Pi_j = \frac{R_{\mathrm{A},j}}{R_{\mathrm{B},j}} = \frac{\Delta T_{\mathrm{A},j}}{\Delta T_{\mathrm{B},j}}, \quad j = 1, 2, \ldots, 4. \tag{3}$$

where j denotes the quadrants and R is the volumetric reaction rate in mol/m^3 s for the catalyst and quadrant indicated. Here, we will only consider the overall average:

$$\Pi = \frac{\langle \Delta T_{\mathrm{A}} \rangle}{\langle \Delta T_{\mathrm{B}} \rangle} \tag{4}$$

The averaging is done with equal weights to all quadrants. This is only valid if the liquid load is equal in all quadrants.

When looking at uniformity of the liquid distribution we start by considering the ideal situation of perfectly uniform flow and equally perfectly uniform catalytic activity. Under such conditions the temperature increase over all quadrants at the same level should be identical. It therefore makes sense to consider the relative temperature increase defined as:

$$\Theta_{i,j} = \frac{T_{i,j} - T_0}{\Delta T_i} \tag{5}$$

where $\Delta T_i = \frac{1}{4}\sum_{j=1}^{4} T_{i,j} - T_0$.

As before it makes sense to have a single overall value that can serve as a non-uniformity index. The measure suggested here is the following:

$$\Phi_i = \sqrt{\frac{\sum_{j=1}^{4}((T_{i,j} - T_0) - \Delta T_i)^2}{(\Delta T_i)^2}} \tag{6}$$

This is zero if the distribution is uniform. Large deviations are also more influential than small ones.

3. Results

3.1. Relative productivity of two different catalysts

As an illustration consider a case in which we want to compare two different methods for catalyst preparation. The productivity of the catalysts will depend on a large number of operational parameters, which can be eliminated from the comparison by carrying out the comparison under as similar conditions as possible. By placing the two catalysts A and B, as indicated in Fig. 1, they are operated under very similar conditions. The small difference in temperature and conversion here is insignificant. Flowrates and liquid distribution, etc. are also very similar. This means that differences in performance can be attributed to differences between the catalysts. The relative productivity of catalyst A over catalyst B is shown in Fig. 2 for the first 18 months on stream. Since the underlying data is logged every 10 s we obtain a band rather than a line. First we note that the width of the band is relatively small compared to the absolute value. This indicates that the relative performance can be estimated within ±10%. We can clearly discriminate between the two catalysts and we see that catalyst A is approximately 30% more active than catalyst B after a few weeks on stream. This difference grows steadily with time and reaches 70% higher productivity after 18 months on stream. It is clear that the aging behavior is different. In this way, it was thus possible to rate the catalyst performance of two different formulations under plant conditions even though they constituted only a minor part of the catalyst inventory.

The large spikes are attributed to short stops. Under non-reacting conditions temperature differences are small compared to measurement noise and the ratio considered has no physical meaning.

3.2. Data filtering

Two examples of the original temperature readings are illustrated in Fig. 3 as their respective temperature increases, $T_{31} - T_0$ and $T_{32} - T_0$. For practical purposes these data are filtered in several steps. A linear interpolation to a common grid in time was followed by a median filter to make it insensitive to outliers. Finally, a symmetric averaging filter was applied to render it more smooth. The resulting filtered signals are shown in the same graph. Henceforth, only the filtered signals are shown.

3.3. Internal consistency

The internal consistency of the temperature readings was validated after 2 months. In connection with a planned stop, the hydrogenation reactor was operated for a few hours with normal liquid flow, but without hydrogen and thus no heat generation. The temperature increases, $T_{i,j} - T_0$, for all

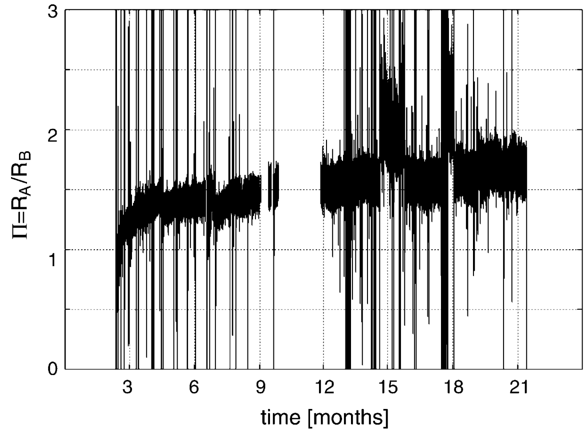

Fig. 2. Relative productivity of two different catalysts for the first 1.5 year on stream.

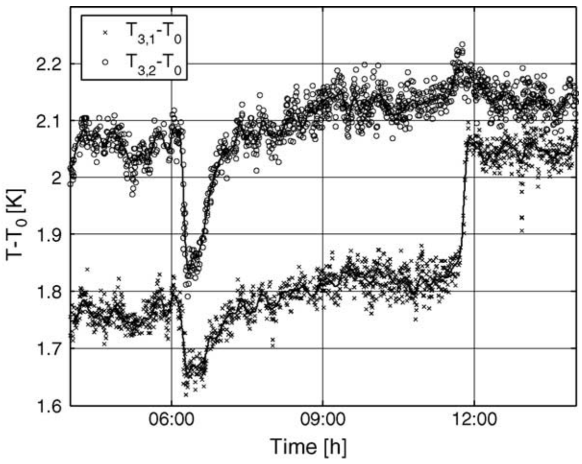

Fig. 3. Illustration of raw data spread and performance of the filtering method employed.

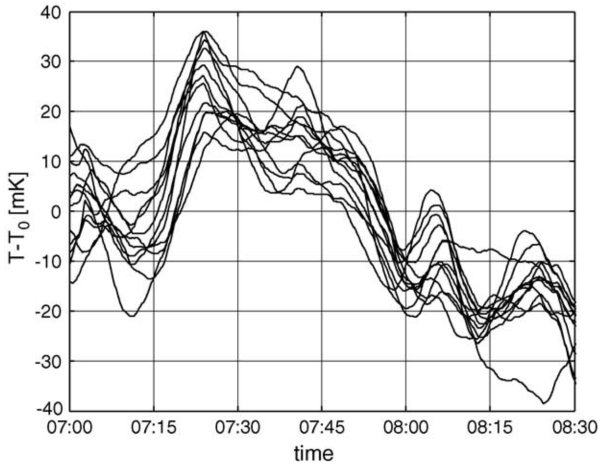

Fig. 4. Internal consistency of temperature readings after 2 months on stream measured with normal loop flow, but without reaction.

sensors indicated in Fig. 1 ($i = 1, 2, 3$; $j = 1, 2, 3, 4$) are shown in Fig. 4. As we can see the internal consistency is very high, typically most sensors are within ±0.01 K from the overall mean. On an absolute scale the errors are larger, but here we only need to pay attention to the temperature differences.

3.4. Flow uniformity

To illustrate how the temperature readings can be used to characterize the flow distribution consider the temperature rise from the feed to the positions in the four quadrants at level 3 ($T_{3,j}$). This is shown in Fig. 5 for a number of hours prior to and after the stop during which the internal consistency was checked. A number of observations can be made:

- Prior to the stop there is a substantial spread in temperature increase, ca. 1.8 K in two quadrants and 2.5 K in two other quadrants. This operational point is stable.
- After the stop the production is gradually increased and a state is reached where all quadrants operate with essentially the same temperature increase.
- During the startup we seem to pass through a number of distinct phases characterized by either very similar or sometimes quite different temperature increases.

The explanation for the latter can be found if we consider the changes to the loop flow rate, Q, performed as part of the trial. The loop flow rate employed was within the stability range as indicated in [1] and [8]. If we denote the normal loop flow rate Q_0 then the quantity $(Q - Q_0)/Q_0$ represents the relative deviation from this normal value. This quantity is plotted together with the non-uniformity index, Φ, in Fig. 6. It is obvious that a small change in loop flow has a pronounced effect on Φ, Moreover, there appears to be an

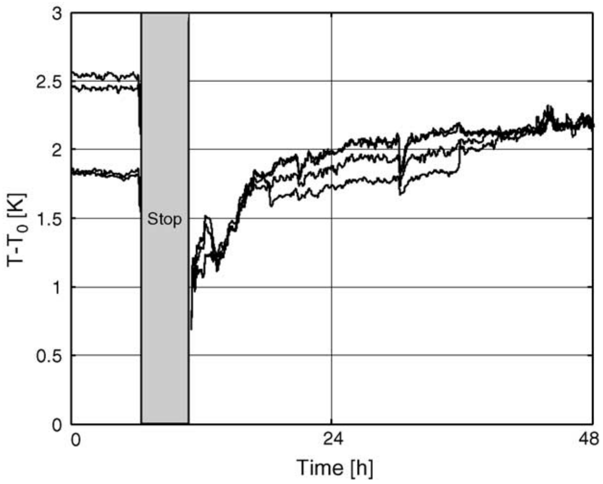

Fig. 5. Temperature increases between feed and third level sensors prior to and after a stop. There is one curve for each of the four quadrants.

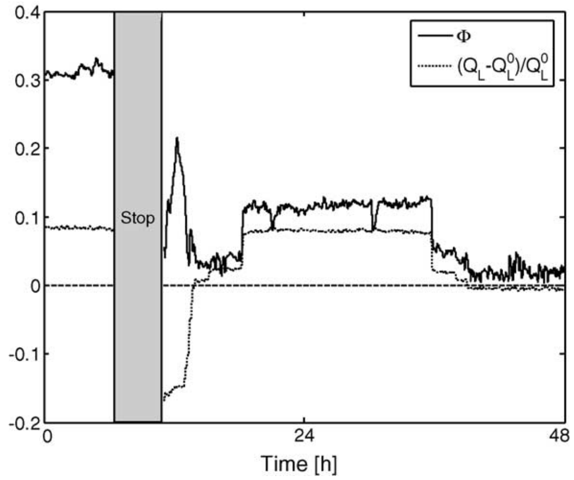

Fig. 6. Non-uniformity index, Φ (topmost curve) and relative loop flow rate prior to and after a stop.

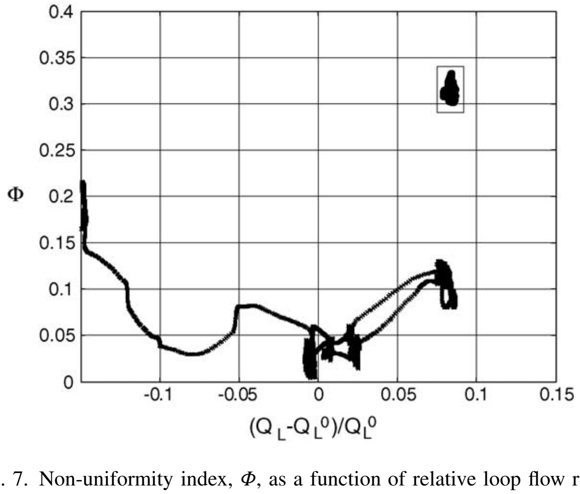

Fig. 7. Non-uniformity index, Φ, as a function of relative loop flow rate. The cluster inside the rectangle to the upper right represents the different operating state before the stop.

optimum loop flow rate that minimizes Φ. This is indicated in Fig. 7. The relatively regular pattern is an artifact caused by the use of filtered data. If we consider the data obtained from the startup (i.e. those outside the rectangle top right) they appear to lie more or less on a parabola with a minimum a few percent below Q_0. However, in order to use this for a full optimization a larger data basis is needed. Moreover, a criteria relating the maldistribution index to the critical performance parameter, e.g. productivity or selectivity, needs to be established. The degree of maldistribution that can be accepted will vary from process to process, e.g. depending on the presence and nature of possible side reactions. The flow rate that minimizes Φ will depend strongly on the design of the distributor system used. Analysis of the kind exemplified above can thus be useful when optimizing distributor systems.

The stable operational points representing the period prior to the stop form its own cluster at the top. This indicates that we may have multiple steady states. This was confirmed by us reaching each of these states several times. The different states are truly stable (no appreciable change after several weeks) and the state reached is determined by the stop/startup procedure employed.

In the case of a non-uniform temperature distribution it is, in principle, not possible to discriminate between non-uniform flow and non-uniform catalytic activity. In practice, we have good reasons to assume high degree of uniformity of the catalytic activity. This assumption is also supported by the fact that a very uniform temperature distribution could be achieved after the startup.

4. Conclusions

By measuring temperatures with a very high internal consistency it is possible to compare local productivities with high accuracy. In this particular case, the superiority of one catalyst preparation method over another could be demonstrated in a large plant reactor, despite the fact that each of the catalyst tested only made up a minor fraction of the catalyst inventory. Differences in deactivation behavior could also be unambiguously demonstrated.

By considering temperature distribution over the cross-section it was possible to identify a strong relationship between a small change of liquid flow rate and the quality of the global distribution uniformity. The practical consequences in terms of reactor performance will depend on the particular system. Moreover, it was possible to show the existence of multiple steady states and relate their existence to the stop/startup procedure.

The method used should be fairly generally applicable as the nature of the chemical process at hand is of little consequence. Normally, only the digits in front of the decimal point of a temperature reading are needed to operate the process satisfactorily. This example shows that lots of useful information about the process can be obtained by carefully considering the first decimal places to the right of that decimal point.

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