On-line analysis of hydrogen peroxide *via* RAMAN spectroscopy. Application to the direct synthesis of H_2O_2 : decomposition reaction

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ABSTRACT

Hydrogen peroxide concentrations in aqueous solutions have been determined by Raman spectrometry. H_2O_2 is a green oxidant agent which direct synthesis from H_2 and O_2 presents a promising alternative to the traditional production process. Raman spectroscopy is a fast, non-destructive and reliable analytical technique for H_2O_2 quantification which avoids the drawbacks of traditional iodometric determinations. A high pressure view cell has been designed to enable the online monitoring of the reactions involved in the direct synthesis process (synthesis, decomposition and hydrogenation) at high pressures. The calibration model produced reproducible and accurate results compared against classic iodometric titration. The feasible use of Raman spectroscopy for real-time quantitative reaction monitoring has been established by analysing the decomposition reaction of H_2O_2 under different conditions.

INTRODUCTION

Hydrogen peroxide is a highly polar component with an extremely oxidant behaviour, which decomposes forming hydroxide radicals with a much higher oxidant potential, only exceeded by fluoride ion [1].

Direct synthesis from H_2 and O_2 has become a promising alternative to the anthraquinone route [2]. In this process, the quantitative determination of the hydrogen peroxide produced is usually carried out by volumetric titration, generally with potassium iodide, potassium permanganate or ceric sulphate [3]. However, this technique implies: a sample extraction which alters the reaction medium, repeatable preparation of the reagents and a long time of analysis. An analytical method that allows the quantification of H_2O_2 in a greener, faster and non-destructive way would be ideal in order to combine it with the direct synthesis process. Several examples of this are found in the literature using spectroscopic methods, usually intended for online determination. Some authors have been able to determine H_2O_2 indirectly by adding a reagent, namely titanyl sulphate [4] or ammonium molybdate [5], which reacts with the peroxide to form a compound that is then measured by UV/VIS spectroscopy. These optical methods, albeit faster and more environmentally friendly than volumetric titrations, still have not given conclusive results in high pressure processes. Since direct synthesis of H_2O_2 is more efficiently carried out under high pressure [6], a method suitable for online direct determination at the reaction pressure would be desirable.

In this work, we successfully carried out the measurement of hydrogen peroxide solutions flowing through a high-pressure cell using a portable Raman spectrometer in order to apply it as monitoring system, and we were able to confirm the possibility of using the solvent which is normally used in the direct synthesis reaction as internal standard for H_2O_2 Raman determination. Aarnoutse and Westerhuis [7] have confirmed that it is possible to use the solvent, particularly 1-methyl-2-pyrrolidinone, as internal standard for Raman monitoring of a liquid-phase Heck reaction. Water was utilised in this work since it is a green and common solvent in the direct synthesis of H_2O_2 [2]. As for inert gases, nitrogen and carbon dioxide were employed when the system was pressurised, both of which are also commonly found in direct synthesis reactions. Due to the extreme importance of side reactions in the overall direct synthesis process, the decomposition reaction of the peroxide has also been studied in the literature [8]. In this work, we have chosen said decomposition reaction to be monitored online and therefore validate the setup and the calibration model.

MATERIALS AND METHODS

1.1 Materials

H_2O_2 (33 wt/v%, reagent grade, Panreac Química S.A.U.) was used to prepare a set of 15 standard solutions (from *ca*. 0.3 to 8.5 wt/v%) for quantitative calibration models. A second set of 10 samples was prepared for validation. Distilled water (Millipore quality) was used as solvent. Spectra were collected immediately after sample preparation to minimise possible errors due to decomposition of the hydrogen peroxide. In order to determine the concentration of the samples, KI (PRS-Codex, Panreac Química S.A.U.), H_2SO_4 (PA-ISO, Panreac Química S.A.U.) and $Na_2S_2O_3{\cdot}5H_2O$ (PA-ACS, Panreac Química S.A.U.) were used for conventional iodometric titration. Industrial grade nitrogen and carbon dioxide were purchased from Carburos Metálicos (Spain) and used without further modification. A commercial 5 wt.% Pd/C (Sigma, Spain) was used for the H_2O_2 decomposition reactions.

1.2 Instrumentation and data processing

All the spectra were obtained with a portable Raman spectrometer BWTEK i-Raman (BWS415) equipped with a 40 mW diode laser emitting at 532 nm with a focal distance in air of 10 mm and an effective focal distance of *ca*. 13.5 mm through the quartz window. The laser system includes a CCD array detector with a thermoelectric cooling (TE-cooling) system which decreases the dark noise allowing a better resolution. The spectral range of the detector is 530 – 700 nm (0 - 4000 cm^{-1} Raman shift) and the best resolution is 5 cm^{-1}.

The equipment was connected to a computer for data collection. Each spectrum was collected using a total acquisition time of 60 s (4 accumulations of 15 s). Data processing of the spectra, including dark noise subtraction, baseline correction and integration, was accomplished using a commercial software package.

1.3 Experimental procedure

Samples were taken from the bottom of a reaction vessel [6] and pumped using a Jasco 2080 HPLC pump through a specifically designed high-pressure SS316 view cell of 3 mL of volume. The cell has a window cap supporting a UV grade quartz window of 20 mm diameter and 10 mm thickness (see Fig. 1). The cell, sealed with one Viton O-ring (id. x od. x thickness, 17.463 mm x 20.638 mm x 3.175 mm) and one Teflon ring (id. x od. x thickness, 11 mm x 20 mm x 2.5 mm), was hydrotested up to 25.0 MPa at room temperature. In order to avoid interference of possible gas bubbles that could be carried in the liquid flow, the high pressure cell was placed upside down and the inlet was lower than the outlet, so that the bubbles would gather on the top. The inlet was 1/16in od. stainless steel tube located just 1 mm above the quartz window to increase the response time of the on-line measurement. In order to minimise background noise, the high pressure cell along with the Raman probe were isolated in an airtight compartment. The H_2O_2 decomposition reactions were carried out under different pressures. In all cases, the initial mixture consisted of 100 mL of an aqueous solution approximately 3 wt/v% H_2O_2 with the appropriate promoters. A first iodometric titration was carried out to confirm the initial concentration, and then the Pd/C catalyst (100 mg) was added to the mixture. Reaction time was 180 minutes since the catalyst was added. The system was pressurised with N_2 or CO_2. Raman spectra were taken automatically every 10 minutes, and 3 samples (1 mL) were extracted for titration at different times (60, 120 and 180 minutes) to confirm the results obtained and thus validate the calibration model.

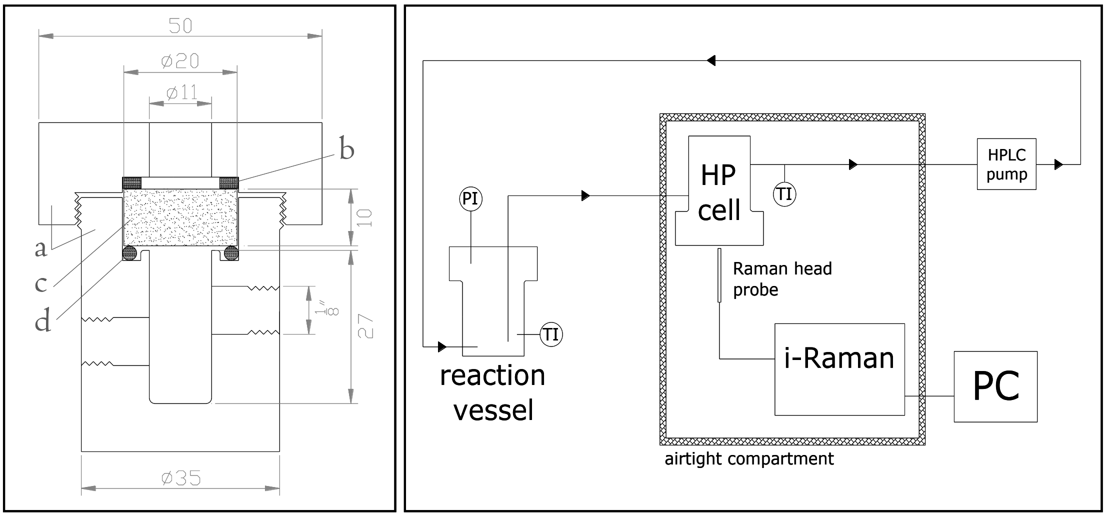

Figure 1. *LEFT*: Design of high pressure cell. The inlet tube (1/16in od) was put near the quartz view window, 1 mm approximate distance (a: 316SS view cell body and window cap; b: Teflon ring; c: quartz window; d: Viton O-ring). *RIGHT*: Layout of the experimental system. The high-pressure cell, laser and CCD sensor were introduced in an airtight compartment.

RESULTS AND DISCUSSION

Calibration of the RAMAN spectra

The calibration curve was built using concentrations ranging from 0.3 to 8.5 wt/v% at room pressure and temperature (*ca.* 22 ºC). The data were adjusted by linear regression.

In order to use the solvent (water) as internal standard, both of its bands, at 1646 and 3400 cm^{-1}, were included in the calibration equation (see Fig. 2). The resulting calibration equation (eq. 1) has a correlation coefficient of 0.991.

$$C = 149.76045 \pm 1.1874 \times \frac{A_{878}}{A_{878} + A_{1646} + A_{3400}} \qquad \text{(eq. 1)}$$

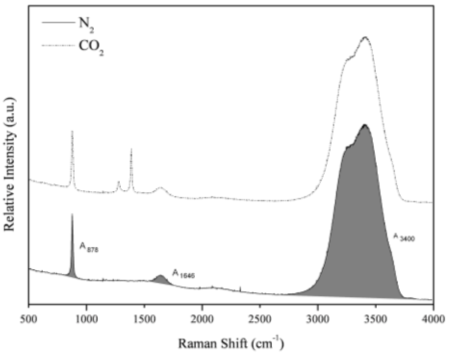

Figure 2. Raman spectra of 2.5 wt/v% H_2O_2 in water and N_2 / CO_2

The values of SEC (standard error of calibration) and %RSEC (relative standard error of calibration) obtained were quite low, being the SEC 0.141 wt/v% and the %RSEC 2.92%, which agrees with previous results for H_2O_2 Raman calibrations and demonstrates the validity of the method proposed (see Fig. 3).

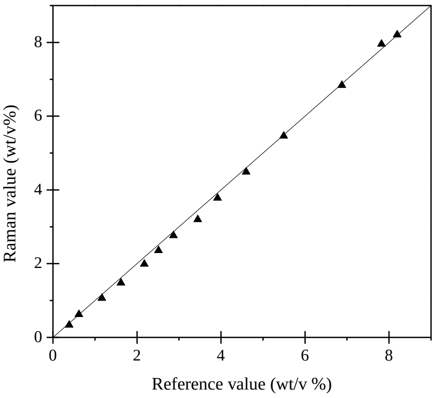

Figure 3. Parity plot of data vs. fit for the calibration model

Influence of the promoters in the decomposition reaction

The reactions for the direct synthesis of H_2O_2 are schematized below:

$$H_2 + O_2 \xrightarrow{k_1} H_2O_2 \qquad \text{(eq. 2)}$$

$$H_2O_2 + H_2 \xrightarrow{k_2} 2\,H_2O \qquad \text{(eq. 3)}$$

$$H_2O_2 \xrightarrow{k_3} H_2O + 0.5\,O_2 \qquad \text{(eq. 4)}$$

$$H_2 + 0.5\,O_2 \xrightarrow{k_4} H_2O \qquad \text{(eq. 5)}$$

In order to test the on-line analytical method proposed, the decomposition reaction (eq. 4) has been studied.

CO_2 acidification effect

When the system is pressurised with N_2 the decomposition takes places faster than when CO_2 is used. In fact, total decomposition is observed after 40 min with N_2 and after 140 min with CO_2. This demonstrates the acidification effect of CO_2 as a protecting agent or promoter.

Halide protection

A similar effect is observed when sodium bromide is added to the reaction medium. In the case of N_2 decomposition, over 60% takes place after 60 min whether with CO_2 it is reduced below 20% after the same period.

External acid protection

The acid protection can also be achieved by the direct addition of protons (using H_3PO_4 or similar). This effect is added to the protection of the Br^- for both N_2 and CO_2, reducing the decomposition below 15% for more than 3 hours, as it can be seen from Fig. 4. In the case of CO_2, the protection is slightly higher than for N_2, due to a cumulative acidification effect, especially at longer reaction times.

The advantage of using CO_2 is that the artificial acid excess is easily eliminated by a simple stripping, while the added protons need to be neutralised using other techniques.

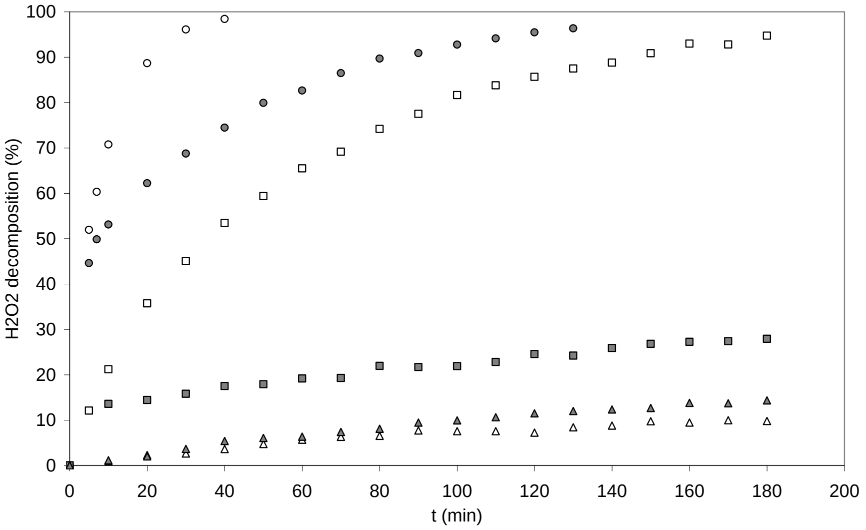

Figure 4. H_2O_2 decomposition for different diluents and promoters: ○ N_2 without additives; ● CO_2 without additives; □ $N_2 + Br^-$; ■ $CO_2 + Br^-$; △ $N_2 + Br^- + H^+$; ▲ $CO_2 + Br^- + H^+$

(reaction conditions: room temperature, 100 mg 5wt% Pd/C, 5 MPa, $[Br^-]=0.004M$, $[H^+]=0.03M$)

Other factors to be studied

Factors such as temperature, Pd load on catalyst and concentration of promoters can also influence the decomposition reaction. These results will be presented in the conference.

CONCLUSIONS

Several goals have been achieved in this work. First, the assembly of an appropriate setup for measuring H_2O_2 concentrations in aqueous solutions using Raman spectroscopy. Second, the successful use of the solvent (water) as internal standard in the measurements and the validation of the calibration model at different pressures.

Third, further validation of the calibration model has been obtained by online monitoring of a decomposition reaction of H_2O_2. And fourth, an insight into the role of different factors influencing the decomposition reaction has been gained. This determination method is a promising alternative for online monitoring of H_2O_2 in a direct synthesis reaction, since it is non intrusive and no sample volume needs to be extracted. As the measurement can be made under the reaction pressure, it does not cause any disturbances in the system. Future work includes coupling this measuring system to a H_2O_2 direct synthesis semi-batch reactor.

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