DOI 10.5162/SMSI2023/A5.1

Measurement of Dissolved Hydrogen in Biogas Fermentation Media

Jens Zosel[1], Rodrigo Renato Retamal Marín[1], Eike Janesch[2], Peter Neubauer[2], Stefan Junne[2,3], Michael Mertig[1,4]
[1] Kurt-Schwabe-Institut für Mess- und Sensortechnik Meinsberg e.V., Waldheim, Germany
[2] Bioprocess Engineering, Institute of Biotechnology, Technische Universität Berlin, Germany
[3] Section for Bioscience and Engineering, Aalborg University Esbjerg, Denmark
4 Physikalische Chemie, Technische Universität Dresden, Dresden, Germany
jens.zosel@ksi-meinsberg.de

Summary:
Hydrogen is a cofactor in many microbial transformation processes and therefore important to achieve a high product yield. The measurement of dissolved hydrogen in biogas processes is complex, because it is conducted at conditions, which may disturb stability and precision of the measured value. A new approach for the measurement of dissolved hydrogen in biogas culture broth by using semiconducting metal oxide gas sensors is presented.

Keywords: metal oxide gas sensor, dissolved hydrogen, biogas culture broth, micro fluidic system

Introduction

Hydrogen (H_2) is a cofactor in many microbial transformation processes and therefore important to achieve a high product yield. It needs to be dissolved in the liquid phase for utilization in cellular transformation. In anaerobic digestion, H_2 occurs usually at partial pressures below 10 Pa [1]. Thus, the provision of cells with sufficient amounts of H_2 is crucial, since it offers only low solubility. This requires a trade-off between expensive improvement of H_2 input rate and its limited availability for a cell.

The measurement of dissolved hydrogen ($H_{2,diss}$) in biogas fermentation media is complex, because it is usually conducted at conditions, which disturb stability and precision of the measured value [2]. These conditions concern biofilm formation on sensitive surfaces as well as hydrogen consumption on surfaces in the fermenter headspace by microbes with access to traces of oxygen. It could be shown in the past that these issues can be circumvented successfully by enabling a membrane-free extraction of dissolved hydrogen ($H_{2,diss}$) into a clean chamber before its detection [3]. This chamber is rinsed with a constantly flowing carrier gas, which is analyzed subsequently for its H_2 concentration ($c(H_2)$). Initially, an automated chromatographic system was used for this task, which is highly sensitive and selective, but it requires a high installation effort. This is associated with costs that exceed the usual scope of biogas production.

This contribution describes a new approach for the measurement of $H_{2,diss}$ in biogas culture broth by using semiconducting metal oxide gas sensors (MOX). These low-cost sensors can be installed with a significantly diminished effort compared to chromatographic systems. Unfortunately, these sensors usually degrade within days when they are in direct contact with biogas. Therefore, within this new approach they are combined with a miniaturized fluidic arrangement based on a small gas-flushable chamber for the MOX.

Methods

The new sensor system consists of a gas supply, a micro-fluidic system with the sensor chamber and a PLC for controlling gas flows and valves and for data logging as shown in Fig. 1.

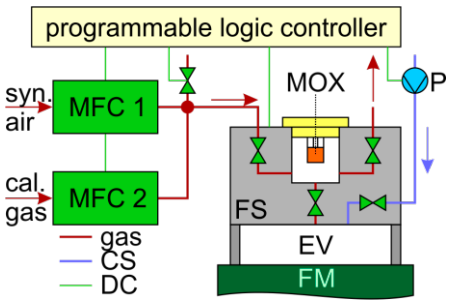

Fig. 1. Scheme of the sensor system: CS = cleaning solution, DC = data/control line, EV = extraction volume, FM = fermentation medium, FS = fluidic system, MFC = mass flow controller, MOX = metal oxide gas sensor, P = pump

The sensor chamber inlet is connected to the gas supply, while the outlet is vented into the environment. A third line connects the sensor chamber to an extraction volume via a solenoid valve. The gas supply provides humidified air or a calibration gas with known c(H_2) during the periods, when the $H_{2,diss}$ in the fermentation media equilibrates with the gas atmosphere in the extraction volume through a membrane-free gas/liquid boundary. After complete equilibration, the flushing gas flow through the sensor chamber is interrupted by closing the valves at the in- and outlet. Subsequently, the connection between sensor chamber and extraction volume is opened for 90 s to allow the extracted H_2 to diffuse into the sensor chamber. The peak of the sensor signal, occurring immediately after this opening, is a stable measure for p($H_{2,diss}$) in the culture broth. After the diffusion step, the extraction volume is filled with fresh air again, and the next equilibration/measurement cycle starts.

Results

The system was characterized in the laboratory in deionized water as model fluid with different concentrations of $H_{2,diss}$. The fluid was held at 25 °C and the partial pressure p($H_{2,diss}$) was adjusted by introducing small gas bubbles of a H_2/N_2 mixture with defined p(H_2) between 1 and 100 Pa.

The resulting calibration curve is shown in Fig. 2 for two independently operating sensor systems. It proves that stable plateau values are achieved at each adjusted value of p($H_{2,diss}$) with a noise below 5 %. The relatively long response time concerns the concentration change in the model fluid, which is significantly longer than the sensor response. The signal is moving back rapidly exactly to the initial 100 Pa level after 120 h measurement, demonstrating a sufficient long-term stability of the sensor.

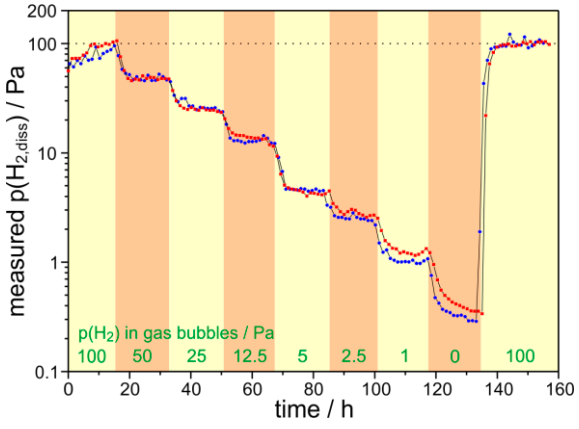

Fig. 2. Calibration curves of two independently operated sensor systems in model media with p($H_{2,diss}$) = 0 … 100 Pa.

After laboratory characterization, the system was installed in a laboratory fermenter and operated for 900 h. The curve in Fig. 3 demonstrates that stable measurements are achievable over this long period.

The peaks of p($H_{2,diss}$) occur immediately after feeding, demonstrating the short sensor response time and the role of H_2 as an intermediate substance in the biogas process and its rapid transfer to the methane producing bacteria. The small fermenter volume of less than 2 liters prevents water cleaning of sensors, due to intolerable dilution of the culture broth. Therefore, the sensor has been cleaned externally, which is also reflected in its signal.

The new sensor system is suited for broad commercialization of dissolved hydrogen monitoring in biotechnological processes.

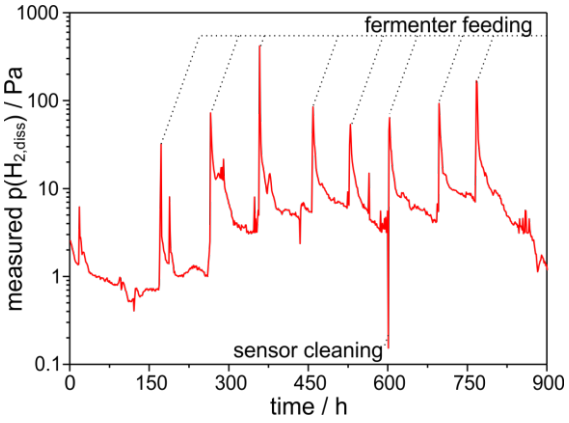

Fig. 3. Long-term measurement of p($H_{2,diss}$) in a laboratory biogas fermenter.

References

[1] X. Wu, H. Yang, L. Guo, Effect of operation parameters on anaerobic fermentation using cow dung as a source of microorganisms, *International Journal of Hydrogen Energy* 35. 46–51, (2010); doi: 10.1016/j.ijhydene.2009.10.039

[2] A. Pauss, G. Andre, M. Perrier, S. Guiot, Liquid-to-gas mass transfer in anaerobic processes: inevitable transfer limitations of methane and hydrogen in the biomethanation process, *Applied and Environmental Microbiology* 56, 1636–1644 (1990); doi: 10.1128/aem.56.6.1636-1644.1990

[3] M. Schelter, J. Zosel, W. Oelßner, M. Mertig, A novel method for measuring dissolved gases in liquids, *Sensors and Actuators B* 193, 113– 120 (2014); doi 10.1016/j.snb.2013.11.070

Acknowledgement

The authors acknowledge funding of the project consortium “ProPhaSep” by the BMWK within the framework program "Biomass energy use", FKZ No. 03EI5409. Das Kurt-Schwabe-Institut Meinsberg wird mitfinanziert durch Steuermittel auf der Grundlage des vom Sächsischen Landtag beschlossenen Haushaltes.