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On the use of electrochemical multi-sensors in biologically charged media

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Abstract. For the investigation and characterisation of liquid media with microorganisms, electrochemical sensors are typically used. Usually the microorganisms are part of the process or cannot be excluded for different reasons. This paper describes the application of various electrodes, which are partly miniaturised and combined with multi-sensor systems for several applications in processes containing microorganisms. The application in industrial bioprocesses like beer brewing and biogas production, and in paper manufacturing, is described. The performance of the multi-sensor systems, and thus their suitability for a contribution to improved process monitoring, is evaluated. The multi-sensor systems represent an interesting tool to enhance monitoring capacities at installed systems without the necessity for huge port installations and offer the possibility to monitor the spatial distribution of gradients. The developed systems presented here allow location-independent measurements in process plants with a variable positioning of the sensors in the industrial reactors.

1 Introduction

Microorganisms play an important role in many industrial processes. On the one hand, they can have a negative influence on the process in which they occur if their presence leads to a contamination. An example is the paper manufacturing process (Kiuru and Karjalainen, 2011). On the other hand, there are many bioprocesses in which microorganisms play an important role in producing valuable goods, like in beer and biogas fermentation. In such cases, highest yield and efficiency can only be achieved if the microbial potential for a bioproduction process is utilised under optimal conditions. To ensure this, among others, monitoring of the cultivation conditions (physical and chemical parameters) becomes necessary. This monitoring should usually be performed online and in situ in order to measure important parameters at any point of the reactor and to detect changes or disturbances early. Consequently, it allows sufficient time for intervention (Wollenberger et al., 2003).

Microbial growth leading to biofilm formation is a major problem in the paper manufacturing process. In consequence, holes, stains or paper web breaks occur. It is assumed that the formation of biofilms is influenced by different factors. These include the supply of nutrients, the pH value, the redox potential, the oxygen content and the temperature. In order to keep a certain control over the growth of the biofilms, biocides are usually used (Pauly and Dietz, 2005). However, the addition of biocides might influence the paper manufacturing process itself (Kiuru and Karjalainen, 2011). Therefore, the lowest amount suitable for circumventing excessive biofilm formation should be used. Hence, the process control by means of electrochemical sensors is not only used for monitoring the microbial growth, but also for monitoring the impact of the application of biocides.

Chemical sensors for the monitoring of industrial processes, for example in a steam power plant (Li, 2008), for drinking water treatment (Hashimoto, 2013), waste water treatment (Volbeda, 2004) and in desalination plants (Hashimoto, 2015), have already been described by different

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authors. Detected parameters in these papers are among others the pH value, the conductivity and the oxygen content, whereby multi-parameter measuring systems are not discussed. Analysis systems for the paper manufacturing industry to determine the moisture content or the cationic charge demand are commercially available (Williamson, 2004).

However, in practice only a few sensors are applied directly in the water circuit for monitoring the paper manufacturing process. The most relevant parameters are the temperature, the conductivity and the pH value. Thereby this refers to fixed installed measuring systems (Kiuru, 2011).

To determine the redox potential, electrochemically electrodes based on noble metals like platinum, gold or palladium are normally used. Thereby, cross-sensitivities against e.g. sulfur-containing compounds have to be taken into consideration. Simultaneously it is possible that the metals themselves can react as catalysts and cause undesired reactions in the medium. Therefore, in this application, a novel redox-sensitive glass-based electrode (Gerlach et al., 2015) which does not show the disadvantages of the noble metal electrodes was used.

Bellin et al. (2014) developed an electrochemical sensor for spatially resolved detection of redox-active metabolites which are formed by microbial biofilms. For the investigation of biofilms in the water circuit of paper manufacturing industries, such a sensor could be suitable. However, in this application, the extreme and constantly varied ambient conditions (composition of the water, flow velocities, etc.) which significantly influenced the growth of the biofilms are problematic. Therefore the described novel robust combination of electrochemical probes has been chosen for the measurement.

Furthermore, the contamination of the measuring system in such complex solutions represents a major problem. In the application presented here, the cleaning was realised by an automatic air purge of the sensor surfaces. The efficiency has been proven in a further paper (Gerlach et al., 2015).

The anaerobic yeast and biogas fermentation processes are the two largest bioprocesses with respect to total product turnover rates. Yeast cells are applied for the production of beer, because they conduct the synthesis of ethanol and carbon dioxide well in the absence of oxygen. However, the brewing process is very complex, so that it relies on many parameters. Even oxygen is required in certain amounts for the cellular growth (O'Rourke, 2002a). Simultaneously, oxygen can negatively affect the quality and stability of the beer during manufacturing and filling (Pöschl, 2006). The enzymes of yeast are responsible for the chemical reactions in a brewing process. They operate optimally only in defined pH and temperature ranges (O'Rourke, 2002b).

In brewing reactors the medium is often not mechanically mixed and homogenised. This causes a high risk of inhomogeneities with regard to different chemical parameters. To detect these inhomogeneities, online measuring systems are suitable devices, especially if they are combined with a variable positioning measuring system for the process characterisation. Consequently, spatially resolved measurements are performed to investigate and compare various areas in the brewing reactor. The movable measuring system has to be as little as possible to avoid the mixing of the medium. Accordingly, only miniaturised sensors can be applied to investigate the required parameters. A further advantage of the miniaturised oxygen sensor is the lower oxygen consumption of the micro-cathode of this probe.

The biogas process is complex, too. Due to various consortia of microorganisms and the non-specific substrate, little is known about the detailed interaction of microorganisms, substrate conversion and product yield, especially at process disturbances or when substrate sources are changed. It is still not clear which parameters can contribute to improved online monitoring due to the little experience of detailed monitoring of the liquid phase in industrial biogas plants. Up to now, there have only been few possibilities to monitor the process, so that many biogas plants work suboptimally (Wiese and König, 2008).

For a large number of biogas plants where measuring systems could already be installed, some usable access points for the introduction of the probes into the fermenters are available. However, the sensing devices are limited in number and are produced in unfavourable sizes. Therefore, a miniaturisation of the electrodes is meaningful for the integration into biogas plants in operation to avoid larger interventions.

Hashimoto (2013, 2015) and Volbeda (2004) have described have described sensors for the determination of pH value, conductivity and oxygen concentration in industrial processes, whereby the sensors are applied individually and not in the form of a multi-parameter probe. Furthermore, the sensors have not been miniaturised, which is essential for the use of small reactor accesses in biogas plants.

There are already developments of electrochemical sensor arrays, e.g. for the online determination of temperature, pH value, dO_2 and biomass concentration (van Leeuwen, 2010). However, they are integrated into micro-bioreactors with a volume of about 100 µL, so that usage in industrial plants is not possible. In addition, Krommenhoek et al. (2008) published results of investigations using microchips with integrated electrochemical sensors to measure the same parameters. These chips were implemented in a well of a 96-microtitre well plate. Betts und Baganz (2006) compared in a review article several micro-bioreactors (for example, based on shake flask, microtitre plate, miniature stirred bioreactor, and stirred tank reactor) with a maximum volume of 500 mL concerning the use of sensors for the determination of pH value, dO_2 and optical density. All developed sensory systems are only suited for small-scale applications. In industrial reactors, e.g. in fermenters of biogas plants, problems have been expected to be caused by pollution or material degradation on the damageable sensor arrays by several substances contained in the media. The results of the studies presented here were carried out in the main digester in a biogas plant in exercise using a miniaturised multi-sensory probe. In addition, the reactions in the hydrolysis basin of this plant were also investigated over months, which is reported elsewhere (Kielhorn et al., 2015).

2 Development and construction of multi-sensor systems

2.1 Multi-sensor measuring system for on-site analysis in the paper industry

An analysis system consisting of a two-part control cabinet (Fig. 1, left) and a multi-sensor probe with a measuring vessel was developed (Fig. 1, middle). The measuring vessel is directly fed with process water from the paper machine. The upper part of the control cabinet includes the components of the electronic and automation equipment. A mini compressor is installed in the lower part. This device produces compressed air to purge the sensitive electrode surfaces by means of nozzles. The compressed air jets are adjusted next to each sensor. The pressure impulses can be activated or deactivated individually. The multi-sensor probe was cleaned manually at the beginning of each measurement. Moreover, the number and duration of the pressure impulses can be limited. The multi-sensor probe includes sensors to measure the dissolved oxygen content, pH value, temperature and redox potential (Table 1; Fig. 1, middle). In addition to a standard platinum electrode, a novel glass-based thick film structure is used for the determination of the redox potential (Fig. 1, right). This electrode currently introduced in Gerlach et al. (2015) is based on electron-conducting glass. Thereby, a number of drawbacks which are connected to the use of noble-metal-based electrodes (especially in biologically charged media) resulting in negative effects on the electrode performance can be avoided. The drawbacks e.g. concern the possible deactivation of the electrode surface under the influence of sulfur-containing compounds and proteins as well as the ability of platinum to catalyse chemical reactions. Additionally, the glass-based structure leads to a lower dependence on the pH value in comparison to the platinum electrode. Furthermore, the analysis system was expanded by an inlet valve upstream from the measuring vessel. As a result, the inlet flow can be stopped in order to measure in a resting solution for a defined period of time.

2.2 Miniaturised multi-sensor probe for use in bioreactors

A multi-sensor for six miniaturised electrodes was designed for biotechnological applications. This device consists of stainless steel and plastic polyetheretherketone (PEEK). These materials are resistant against typical cultivation conditions and media components. The screwable protective hood protects the electrodes against mechanical influences and offers the possibility to change the electrodes separately.

Figure 1. Left: control cabinet of the measuring system for monitoring process water; middle: multi-sensor probe with different electrodes and compressed air jets and the measuring vessel; right: redox glass electrode.

The multi-sensor probes are individually adapted to the different fields of application.

2.2.1 Miniaturised multi-sensor probe for brewing reactors

The developed probe is approximately 140 mm long and it has a diameter of 30 mm (Fig. 2, left). This device contains electrodes for measuring the dissolved carbon dioxide and oxygen, the pH value, the redox potential and the temperature (Fig. 2, right; Table 2). To determine the pH value and the redox potential, a common silver chloride reference electrode is applied. All electrodes were fabricated in-house. The protective hood is equipped with a margin of a few millimetres (Fig. 2, middle) to install a second housing, which includes a pressure sensor.

2.2.2 Miniaturised multi-sensor probe for biogas digesters

The multi-sensor probe (Fig. 3, left), which is used in digesters of biogas plants, has similar dimensions to the previously mentioned one. It consists of the same materials. The stainless steel device includes a temperature probe, a pH electrode, an electrode for the determination of redox potentials and an electrochemical reference electrode (Fig. 3, right; Table 2). Depending on the used measurement device, either one common reference electrode for the determination of pH value and redox potential is applied or two separate reference electrodes are required.

3 Results and discussion

The developed multi-sensor measuring systems are tested in practical applications. Their monitoring abilities in the

Table 1. Overview of the sensors installed in the on-site analysis system.

Sensor/electrode	Design	Measuring principle; manufacturer
Oxygen	Cylindrical; platinum cathode and Ag/AgCl anode; gas-permeable membrane	Amperometric; Sensortechnik Meinsberg GmbH
pH (glass)	Cylindrical; spherical glass membrane; platinum wire with sintered silver chloride body; glass electrode is filled with a KCl-containing electrolyte.	Potentiometric; Kurt-Schwabe-Institut (KSI)
Redox (Pt)	Cylindrical; platinum wire embedded in glass	Potentiometric; KSI
Redox (glass)	Thick film with glass membrane	Potentiometric; KSI
Reference	Cylindrical; Ag/AgCl electrode and KCl gel electrolyte; porous ceramic diaphragm	Reference electrode for potentiometric measurements (pH and redox potential); KSI
Temperature	Cylindrical; platinum (Pt 1000)	Resistance thermometer; KSI

Table 2. Overview of the miniaturised sensors installed in the multi-sensor system.

Sensor/electrode	Design	Measuring principle
Oxygen	Cylindrical (length: 40 mm; diameter: 4 mm); three electrode system (working, counter and reference electrode); micro-cathode (diameter: 30 µm); screwable cup with gas-permeable polypropylene membrane	Amperometric (defined working potential = 800 mV)
pH (glass)	Cylindrical (length: 40 mm; diameter: 3 mm); spherical glass membrane; platinum wire with sintered silver chloride body; glass electrode is filled with KCl-containing electrolyte.	Potentiometric
Redox (Pt)	Cylindrical (length: 40 mm; diameter: 4 mm); platinum wire embedded in glass	Potentiometric
Carbon dioxide	Cylindrical (length: 70 mm; diameter: 7 mm); two electrode system (pH and reference electrode); gas-permeable polymethylpentene membrane; inner pH electrode (glass body) is filled with buffer solution; electrolyte cup contains glycol solution.	Potentiometric (based on pH measurement)
Reference	Cylindrical (length: 40 mm; diameter: 4 mm); Ag/AgCl electrode with KCl inner electrolyte; screwable cup with porous aluminium oxide ceramics diaphragm	Reference electrode for potentiometric measurements (pH and redox potential)
Temperature	Cylindrical (length: 40 mm; diameter: 4 mm); platinum (Pt 1000)	Resistance thermometer

applied environments are evaluated for several weeks and months, respectively.

3.1 Multi-sensor system for application in the paper industry

The multi-sensor measuring system was applied in a paper mill for several months. In the following, two measurement examples of this practical testing are explained.

In Fig. 4, a part of a long-term measurement with the multi-sensor probe in a paper mill is shown. Thereby, the automatic cleaning of the electrodes was performed by air streams every 12 h (3.25, 15.25 h, etc.). The redox potentials, which are measured with a platinum electrode as well as with a glass-based structure, reached a constant level within a few hours. However, the platinum electrode responded to the first pressure impulse (cleaning by air stream) and detected a de-

Figure 2. Left: multi-sensor probe; middle: top view of the multi-sensor probe; right: miniaturised electrodes (from left to right: carbon dioxide sensor, oxygen sensor, pH electrode, redox electrode, reference, temperature probe).

crease of 0.035 V. The following purifications caused even greater changes in the redox potential. The curve progression of the redox glass electrode reflected the several air cleaning procedures after the third event only. The measured value started to decrease slightly approximately 4 h before the purification (27.25 h). The base level was reached again within a few minutes after purification. A similar behaviour was observed at the two following cleaning intervals at 39.25 and 51.25 h. It was determined that the decrease in the redox potential curve (glass electrode) prior to the individual purification steps and accordingly the increase in the redox potential after the cleaning became greater over time. The pH value reacted similarly. It showed the same behaviour as the redox glass electrode, starting with the third cleaning interval. This indicates a relevant biofilm formation after approximately 24 h, which covered the sensitive surfaces of the electrodes and the measuring vessel. The steadily increasing changes in the parameters redox potential (glass-based electrode) and pH value over time showed the growing microbial contamination in the measuring vessel. Moreover, the growth of the biofilm on the electrode surfaces as well as in the measuring vessel was faster after each purification step over time. This can be seen in the slow decrease in the measuring values. This drop in the graph started earlier after each cleaning.

In Fig. 5, the redox potential, the oxygen content and the temperature measured in 54 days are shown for a period of 2 days. Thereby, the purification by means of air was automatically performed every 6 h (0.25, 6.25 h, etc.), followed by a 1 h interruption of the inlet flow. The temperature of the process water of the paper machine was about 313 K. This parameter decreased during the 1 h stop, because the solution in the measuring vessel cooled down by 3 to 4 K due to the lower ambient temperature. The oxygen concentration of the solution was varied in the range of 70–90 %. Naturally, the oxygen content decreased significantly during the inlet stop. Additionally, a dependence on the measurement duration was recognisable. The oxygen concentration further decreased with each additional interruption of the inlet. No oxygen was detectable for a few minutes during the sixth stop. Hereafter, the time in which the oxygen concentration was equal to zero increased clearly. The redox potential (glass-based electrode) showed nearly a constant level (0.14–0.16 V) apart from the inlet stops. However, the decrease in the redox potential became larger during the stationary phase in the course of the observation. The measurement curve of the platinum electrode showed a remarkably different behaviour. The measurements of the redox potential raised up to a maximum value during the first five inlet stops. As expected, the measurement of the redox potential decreased significantly each time the flow through the measuring vessel was recovered. However, in the following three interruptions, only smaller rises could be detected. Furthermore, the increase in the potential began earlier compared to the first inlet resting phases and the decrease was considerably reduced due to the activation of the flow.

The behaviour of the parameters redox potential (glass-based electrode) and oxygen concentration described here in correlation with the purification steps and the interruptions allow the conclusion that by means of both parameters the microbial growth in the measuring vessel can be monitored. If aerobic microorganisms are present in the measurement solution, they consume the oxygen, which is available. This effect was shown by the inlet stops. Simultaneously, changes in the redox potential (glass-based electrode), which also refer to the bacterial growth in the liquid medium, could be detected.

3.2 Miniaturised multi-sensor probe for bioreactors

3.2.1 Brewing reactors

The long-time stability and accuracy of the sensors were tested in several fermentations at the laboratory scale (4 L) before the long-time application at laboratory (12 L) and pilot scale (200 L).

The wort solution that served as an investigation medium consisted of water, various carbohydrates, proteins, minerals and bitter substances. For all processes the brewing was inoculated with bottom fermenting yeast, fermenting at temperatures between 283 and 285 K, and was not stirred. The sensors were calibrated in standard solutions at 285 K. The processes were monitored by the sensor probe during the whole fermentation time. In order to determine the measurement accuracy and deviation over time, the sensors were inserted once per day into the following standard solutions: pH buffers, oxygen-saturated water, autoclaved wort, and standard buffers with different redox potentials (Table 3). In this table the measured deviations after times of 65 and 120 h are also shown. Drifts are given for the pH electrode in pH units, for the oxygen sensor in % air saturation, for the CO_2 sensor in $g\,L^{-1}$ and for the redox sensor in mV which resulted during the operating time. The deviation of the pH measurement after 120 h is much lower than after 65 h. This can be ex-

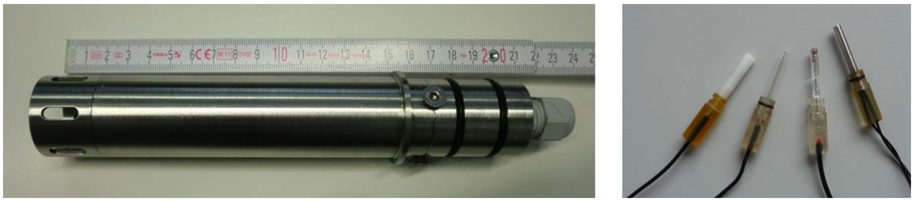

Figure 3. Left: multi-sensor probe; right: miniaturised electrodes (from left to right: reference, redox, pH electrode, temperature probe).

Table 3. Absolute deviation over fermentation time.

Time frame	pH (in buffer solutions)		dO_2 (%) (in O_2 saturated water)	dCO_2 ($g\,L^{-1}$) (in autoclaved wort)	Redox potential (mV) (in standard solutions)	
	pH = 4	pH = 7			250 mV	124 mV
65 h	0.54	0.78	0.37	0.65	2.11	1.11
120 h	0.09	0.27	3.29	0.28	7.61	2.87

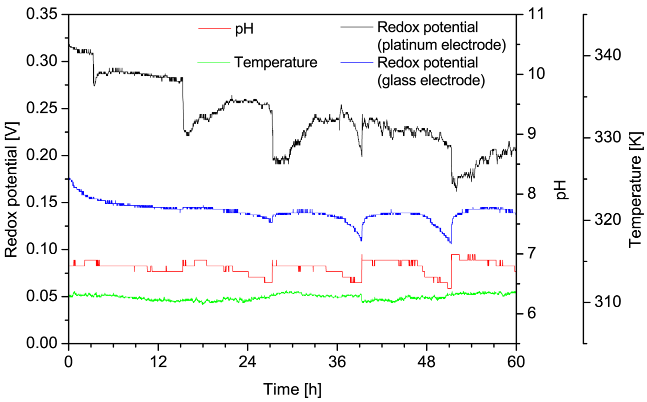

Figure 4. Influence of the air cleaning every 12 h on the parameters redox potential, pH value and temperature during a measurement in the process water of a paper industry.

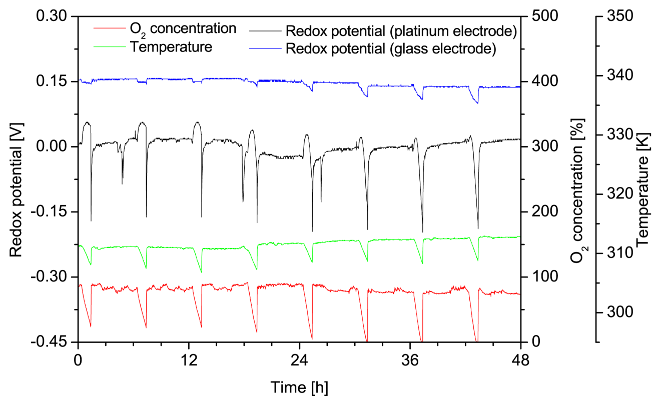

Figure 5. Influence of the air cleaning and the inlet stops (every 6 h) on the parameters redox potential, oxygen content and temperature during a measurement in the process water of a paper industry.

plained by a short-term contamination of the pH chain. During the fermentation this disturbance became detached from the electrode surface. The observed deviations of the redox electrode (less than 8 mV) are almost negligible.

For the estimation of the stability of the pressure sensor, the liquid column of the medium and hence the pressure due to the static head of liquids were used as a reference (data not shown).

The results of two experiments are exemplary displayed in Table 3. The values represent the difference between value measured at the onset and the end of the fermentation in the corresponding reference solution. From these results it can be assumed that the sensor probe can be applied during a brewing process over a fermentation time of 120 h without additional recalibration during the process.

The applicability of the pH sensor could also be proven by the comparison of the *online* measurements with the *offline* controls (measured by a common glass electrode) during a fermentation process at the pilot scale (Fig. 6). The values correspond to each other over a time of 103 h.

The application of the multi-sensor system in a brewing reactor at the pilot scale (volume = 150 L) for 100 h is shown in Fig. 7. At the start of the measurement (Fig. 8), a rapid decline of the oxygen concentration until a level below 1 mg L^{-1} combined with a decrease in the redox potential could be detected. The reason is the oxygen consumption of the yeast cells. Conversely, the carbon dioxide concentration increased and reached a value of 1.1g L^{-1} after 5 h. The pH value decreased continuously from 5.2 to 4.0 (Fig. 7), because of the carbon dioxide produced by the yeast cells. Carbon dioxide is dissolved in the medium, leading to carbonic acid formation and subsequent decomposition to hydrogen ions. The course of the redox potential (Fig. 7) detected by a platinum electrode presents distinctive changes,

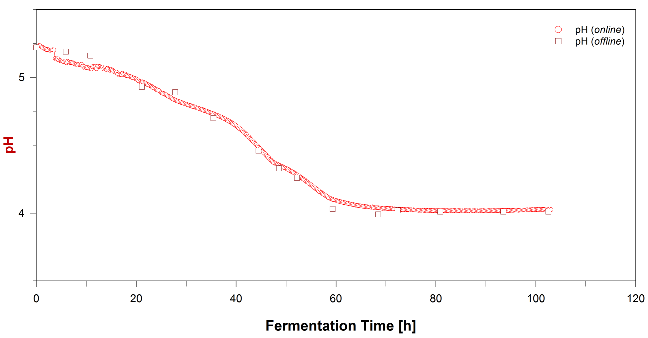

Figure 6. Course of the pH value, monitored online and offline during a fermentation process at the pilot scale (volume: 150 L; 294 K).

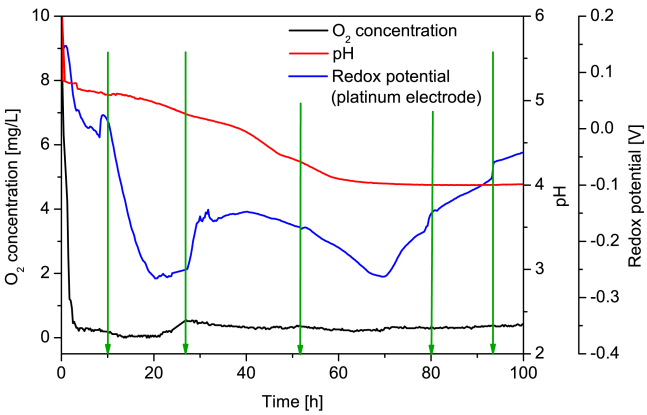

Figure 7. Course of the oxygen concentration, the pH value and the redox potential during a yeast fermentation over 100 h in a laboratory reactor; green arrows: movement of the sensor probe (volume: 150 L; 294 K).

which mostly refer to inhomogeneities of the reactor volume or to changes in the position of the multi-sensor probe in the reactor. Some of these events are shown in the courses of the parameters, e.g. after about 10, 27, 52, 80 and 93 h, when sampling was also performed. This was reflected in the redox potential values (Fig. 7, green marking).

3.2.2 Biogas digester

Measurements were performed at a pilot biogas plant. Several gas-tight locks were accessible from the top part of the bioreactor, which was made of concrete. The locks enabled a vertical measurement applying the multi-sensor probe. The measuring unit was attached to a 6 m long guide tube (Fig. 9, left), which could be attached to different sampling spots (Fig. 9, right). Consecutively, the investigations at two measuring positions are described.

At one sampling spot, which is positioned approximately centrally between the outer edge and the middle of the digester, changes in the pH value and temperature are not recognisable at different immersion depths (Fig. 10). Agita-

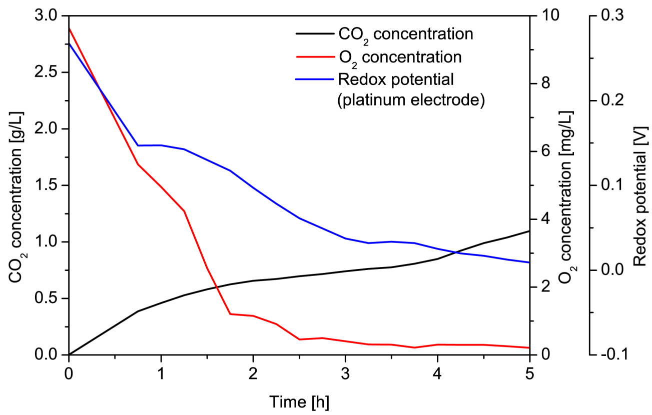

Figure 8. Course of the carbon dioxide and oxygen concentration as well as the redox potential in the start phase of a yeast fermentation in a laboratory reactor (volume: 150 L; 294 K).

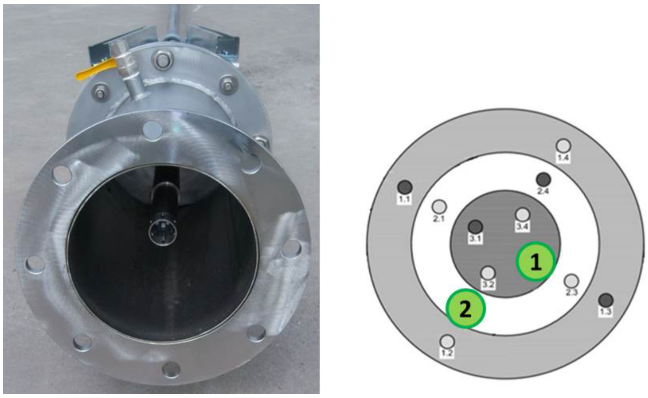

Figure 9. Left: multi-sensor probe in the device to install on a gas-tight lock; right: schematic drawing of the two used fermenter entries by means of gas-tight locks.

tion had no noticeable effect on these two parameters. During the measurement, the temperature curve fluctuated only up to 0.1 K. The average temperature was 325 K. The pH value varied in the range from 7.85 to 7.9. Accordingly, at this spot, a good homogeneity could be assumed with regard to the parameters temperature and pH value up to a depth of 3 m. In contrast, by means of the redox potential (platinum electrode), the change in the immersion depth led to a change in the measured redox potential. It varied in the range of 0.475–0.5 V. The immersion depths 1, 2 and 3 m are surveyed twice, whereby at the immersion depths of 1 and 3 m the repeated measurements had similar values.

The investigation of a second sampling spot (data not shown), which is positioned closely to the middle of the digester, has revealed similar pH and temperature values as at the previously described spot. The temperature was 325 K on average. The pH value varied in the range of 7.85–7.89. Again, the redox potential measurements were influenced by the immersion depths in a range between −0.472 and

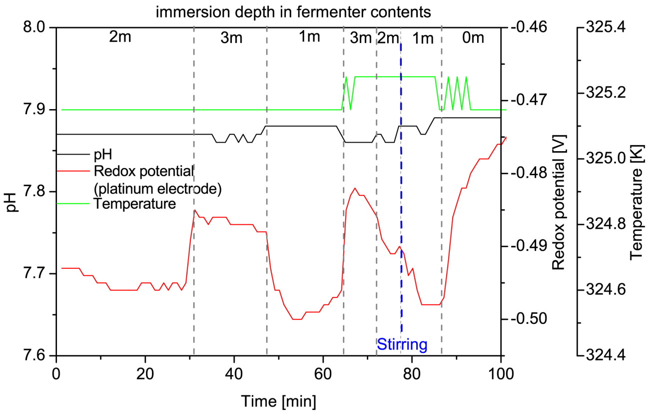

Figure 10. Course of the pH value, the redox potential and the temperature depending on the immersion depth of the measuring probe at test position 2 of the digester.

−0.494 V. Each position of this sampling spot was examined twice, whereby the redox potentials at the immersion depths of 1 and 3 m were nearly reproducible.

After several short-time investigations, the multi-sensor probe was inserted into a second fermenter of the biogas plant for 42 days (data not shown). The installed miniaturised electrodes were calibrated at 323 K before and after the mentioned applications. The testing of the pH electrode against a silver/silver-chloride reference electrode (SSE) showed a negligible change in the sensitivity of 0.3 mV/pH and a decrease in the asymmetry potential of 0.8 mV. The redox electrode was also checked against a SSE, whereby the changes were only several mV. The calibration of both reference electrodes against a SSE resulted in potential increases of 31 and 40 mV, respectively. This corresponds to drifts of 0.7 or 1 mV per day, which were considered mathematically.

In the presented short-time measurements, a dependence of the redox potential on the immersion depth could be detected. Thereby it was remarkable that the present influence by the immersion depth ensured that the redox potential reached strongly negative levels at lower immersion depths.

4 Conclusions

Based on three different examples, we were able to demonstrate that several parameters like pH value, redox potential and temperature are necessary to characterise biological media or solutions, which are contaminated with microorganisms and chemicals. Depending on the application, it is useful to add further appropriate parameters and to choose the dimension of the measuring system. If it is important to disturb the test solution like in brewing reactors as little as possible and to prevent mixing, the present miniaturised multi-sensor probe can be utilised. Their application may also be useful in great fermenters like in biogas plants or brewing reactors, because the reactors normally have only few access points and these entries are limited due to their size. In many cases, little effort was put into the installation of sensors in the liquid phase; thus, the later integration of sensors during operation requires a certain restriction in dimensions of them. However, if the entrance to the test medium is not limited, the miniaturisation of the measuring system is not necessary. Therefore, greater electrodes, which are more robust and stable over long times due to larger electrolyte volumes, can be used. That is why this system is employed in very demanding conditions, such as the paper manufacturing process. Thereby, huge amounts of process water, which contains different chemical and biocidal substances, are available. Furthermore, it is contaminated with microorganisms, so that the development of an automatic cleaning procedure for the sensors was necessary.

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