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REVIEW

Sensor systems, electronic tongues and electronic noses, for the monitoring of biotechnological processes

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Abstract Production of biofuel is based on the conversion by microorganisms of complex organic substrates into the methane or ethanol, which are consequently used as energy sources. Real time monitoring of the fermented media composition is of paramount for the effectiveness of the whole process. However, despite the fact that products worth billions of dollars are produced through fermentation processes annually, analytical instruments used for these processes' monitoring remain relatively primitive. Established laboratory techniques produce exhaustive information about media composition but analysis is often quite time-consuming, expensive, requires skilled personnel and hardly can be automated. Lack of on-line sensors for the fermentation monitoring is commonly stressed in the literature. One of the techniques particularly suitable for this purpose is chemical sensors. Such features as low prices, relatively simple instrumentation, minimal sample preparation and easy automation of measurements make chemical sensors an attractive tool for industrial process control. However, practical use of chemical sensors in complex media is often hindered by their insufficient selectivity. For example, only pH and oxygen probes are routinely used in bio-reactors. One of the emerging approaches permitting to overcome the selectivity problems is the use of systems instead of discrete sensors. Such systems for liquid and gas analysis were named electronic tongues and electronic noses correspondingly. They are capable to perform both quantitative analysis (components' concentrations) and classification or recognition of multicomponent media. This review presents recent achievements in the R&D and applications of electronic tongues and noses to the monitoring of biotechnological processes.

Keywords Multisensor systems · Biofuel production · Biomimetic sensors · Electronic tongue · Electronic nose · Fermentation monitoring

Background: monitoring of biofuel production processes

Climate change is one of the main environmental concerns of our time and significant attention is paid to the reduction and stabilization of the greenhouse gases concentration in the atmosphere. That can be achieved by the transfer from the fossil fuels to the renewable sources of energy, one of which is biofuel produced from biomass. Though estimates of the biomass contribution to the future energy systems vary widely [1], importance of biomass as a sustainable energy source and significant increase of its use in the coming years is generally accepted [2]. Biofuel production is based on anaerobic conversion by microorganisms of complex organic substrates (i.e., cattle manure, food industry wastes, etc.) into the methane or ethanol, which are consequently used as energy sources. Anaerobic digestion is a complicated process depending upon a complex interaction between various groups of bacteria. A fine balance between these groups is necessary for successful digestion giving a large methane yield. The process conditions define the development of the digestion. In a situation of imbalance, an accumulation of hydrogen and other intermediates are likely to occur giving rise to inhibitions and metabolic shifts. Indeed, the entire process can stop totally if the

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imbalance is allowed to proceed. The following factors may lead to the process imbalance: hydraulic overloading, organic overloading, and the presence of inhibitory concentrations of toxic material in the reactor, e.g., heavy metals, ammonia, organic solvents, etc. Several parameters are suggested to be important in the anaerobic digestion process including concentrations of hydrogen, carbon dioxide, methane, volatile fatty acids, ammonia, carbon/nitrogen ratio, pH and alkalinity. Established laboratory techniques such as HPLC, gas chromatography, etc. are capable of producing exhaustive information about media composition but analysis is often quite time-consuming, expensive, requires skilled personnel and hardly can be automated. Currently, chemical analysis of biomass from digesting tanks is performed in the laboratory few times a month and therefore gives no opportunity to correct the process. The principal means of controlling the biogas production process is still by feeding the reactor with appropriate type of raw material. Therefore, real time detection of the key substances in the biomass and monitoring of the changes in its compositions occurring during the process are of paramount for the effective functioning of a digester.

Analytical tools for the on-line process control remain relatively primitive up to date. It is worth noting that lack of analytical instruments is a common problem for all biotechnological industry despite the fact that products worth billions of dollars are produced through fermentation processes annually. Lack of on-line sensors for the monitoring of the fermentation processes is commonly stressed in the literature [3, 4]. The only chemical parameters being routinely measured in the bioreactors are pH and pO_2 [5, 6]. Recently gas analyzers that may be used at-line for the detection of biogas (CO and CH_4), H_2, O_2 and CO_2 in the headspace of the bioreactor were suggested [7].

Several analytical instruments were proposed for on-line monitoring of the fermentation processes and anaerobic digestion in particular. The most important are NIR spectroscopy and image analysis. Both techniques are non-destructive, rapid and require no sample preparation, which make them quite attractive for the real-time process follow-up. Being non-contact techniques, both NIR and image analysis are devoid of such problems as contamination of the probe by the broth compounds and sterilization. NIR spectroscopy is nowadays widely used in agricultural, food and pharmaceutical industries as quality control tool given that problems with instrumental drift and calibration stability are solved. Artificial vision or image analysis makes use of images collected using CCD or other type of camera. This is a new technique that has not yet been widely applied in the industry. Both NIR spectroscopy and image analysis require relatively complex statistical methods for the data processing and modeling especially in the case of image analysis. It should be noted that wider application of NIR in biotechnological industry is impeded by the complexity of analyzed media and the fact that only relatively high concentrations can be quantified using this technique [8, 9]. NIR and image analysis were demonstrated to be feasible for off-line and at-line monitoring of the anaerobic digestion process [10–13].

One of the analytical instruments particularly suitable for the tasks of on-line or at-line process monitoring are chemical sensors. Not surprisingly, on-line probes that are used currently in bioreactors are chemical sensors, e.g., pH and pO_2 probes. Known advantages of the chemical sensors include the possibility to perform measurements in real time, easy automation of measurements and relative simplicity and low price of the required instrumentation. However, practical application of the sensors for on-line measurements in bioreactors is limited by rather strict requirements that sensor should meet to be used for biotechnological process control [3]. The common problems with on-line sensors are contamination and surface adsorption of organic matter from the reactor that lead to the drift or change of the response parameters (baseline and sensitivity). Furthermore, sensors should not require re-calibration for prolonged periods of time or re-calibration procedure should not compromise the process. Sensors should be able to measure substances of interest in the range of their variation during the process that is to have adequate dynamic ranges and detection limits. Sensors should be able to endure sterilization procedure without deterioration of their performance. Sensors should possess sufficient selectivity towards measured substance to be capable of carrying out determination in the complex environment such as fermentation broth where several other compounds are present often in the high concentrations. Just a few of the commercially available sensors meet those stiff conditions and those are the ones already used in bioreactors as was described before.

A promising approach for solving at least some of the problems related to the measurements with sensors in multicomponent media was suggested about two decades ago. It consists in the use of the arrays of sensors or multisensor systems instead of discrete sensors. The present paper gives a short overview of multisensor systems or chemical sensors' array and discusses their applications to the follow-up of the biotechnological process including biogas production.

Multisensor systems

Concept of biomimetic multisensor systems

Chemical sensors are widely known analytical instruments. Some of them, such as ion-selective electrodes are almost one hundreds years old. The first potentiometric sensor—ion-selective electrode (ISE)—was glass pH-selective one suggested in 1909 by Haber and Klemensiewicz. It is still, with minor modifications, the most selective and most widely used liquid sensor. Traditionally, R&D in the field of chemical sensors as well as analytical instruments was aimed at obtaining the highest possible selectivity to an analyte. As a result, a number of highly selective sensing materials for ISEs were developed and applied to practical tasks. However, the number of selective sensors available for analytical purposes still remains significantly restricted in spite of hectic efforts of many researchers. One of the possible ways to deal with insufficient selectivity is utilization of not only highly selective but also of partially selective or cross-sensitive sensors, comprised into sensor arrays. Such sensors may respond to several substances in the multicomponent media and therefore produce complex outputs that need multivariate data analysis or pattern recognition techniques for their interpretation. This idea was firstly implemented in the systems for gas analysis, widely known now as "electronic noses" [14]. Later liquid analyzers based on the same principles were developed. They were called "taste sensor" [15] or "electronic tongue" [16].

Development of the electronic nose and, to less extent, of the electronic tongue was obviously inspired by biological sensory systems, first of all by mammalian olfaction. Olfactory system of mammals consists of a big number of non-specific receptors (sensors) that respond to volatile compounds and transfer stimuli via nervous system to the brain, where the signal pattern is processed. Finally, mammalians are capable to recognize thousands of odors with very low sensitivity threshold to some components in spite of non-selectivity and relatively high detection limit of each individual receptor. Impressive performance of the olfactory system is achieved due to its architecture: a wide set of different receptors and specific processing of their signals first in the peripheral nervous system and finally in the brain. The sense of taste in mammalians functions similar to the olfaction but smaller number of receptors were described compared to the olfaction. Therefore design of both electronic tongue and electronic nose was mimicking olfaction that is combination of an array of non-specific or cross-sensitive sensors with data processing by pattern recognition methods. Again, similar to biology, one of the most often used data processing methods is an artificial neural network (ANN) [17], which algorithms are simplified mathematical representation of the learning, memorizing and recognition processes occurring in the human brain [18]. Classical statistical methods such as principal component and factor analysis, multivariate regression techniques, etc. [19, 20] are also widely used for processing of the data from multisensor systems.

According to [14], the first attempt to develop an odor detection system dates back to the early 60s [21]. However, the history of electronic nose as an intelligent multisensor system started in 1982 after the seminal work by Persaud and Dodd [22]. Since that time several groups added to development and application of such devices. Since the early 90s the same approach was applied to the liquid sensors leading to the development of the electronic tongue or a taste sensor, as the first such system was called [15]. The first electronic tongue systems were based on the potentiometric sensors [15, 16] but later other types of sensors were employed as well. Currently, sensors based on a variety of transduction principles are used in both the electronic nose and electronic tongue systems including electrochemical (potentiometric, amperometric, impedimetric), gravimetric (surface-acoustic wave, quartz crystal microbalance, etc.), optical (fluorescence, etc.), etc. The main types of chemical sensors used in biomimetic systems together with most typical applications are listed in the Table 1. Chemical sensors can be defined as analytical instrument combining sensitive layer undergoing chemical changes during the contact with analyte and transducer transforming this chemical signal into physical one, which is registered. Classification of chemical sensors presented in the Table 1 is based on the type of transducer. Thorough up to date reviews of the electronic tongue systems can be found in [23, 25] and of electronic noses in [26, 27, 46].

Though design of the both electronic tongues and noses was inspired by their biological counterparts, one should be careful in drawing parallels between natural and artificial sensory systems. Besides the fact that electronic noses are used for measuring gases and electronic tongues for the measurements in liquid media, these devices bear very little resemblance to the natural sensory systems. Firstly, sensors used in electronic noses and electronic tongues are based on the different sensing materials and often measuring principles as well, neither of which having anything in common with biological receptors. As a consequence characteristics and performance of biological and artificial gas and liquid sensors differ significantly with respect to sensitivity, selectivity and detection limits. In mammals performance of the olfaction is superior to the one of the sense of taste. Situation with artificial sensors is different. For example liquid sensors usually have lower detection limits, which can in some cases go down to ppb or even ppt levels [e.g., 47, 48], and higher selectivity compared to the gas ones. Evidently, despite the names "nose" and "tongue" both instruments are applicable to the measurements in the inedible or toxic environments. Electronic noses usually provide for the recognition and classification of the gas mixtures and in some cases for the semi-quantitative analysis while electronic tongues are capable of performing both recognition of complex liquids and quantifications of the components. Both

Table 1 Sensors for the electronic tongues and electronic noses

Transduction mode	Analyzed medium	Sensing materials	Analytes and applications
Potentiometric	Liquid	Plasticized organic polymers modified by ionophores; chalcogenide glasses; noble metals [23–25]	Alkali and alkali-earth cations, inorganic anions, organic acids, phenols, taste substances, transition metals, rare earth metals, etc.; classification and recognition of foodstuffs, taste assessment of foodstuffs and pharmaceuticals, etc.
Amperometric	Gas	Catalytic layers of noble metals with high surface area [26, 27]	Detection of toxic gases (Cl_2, CO, CO_2, HCl, HCN, HF, H_2S, NH_3, CH_3NHNH_2, NO, NO_2, PH_3, SO_2, etc.)
	Liquid	Noble metals (Pt, Pd, Au, etc.) [28], carbon paste electrodes modified by phthalocyanines, doped polypyrrol films [29], glassy carbon electrodes	Classification and recognition of foodstuffs, molds, quality control of potable and waste waters (qualitative) Classification and recognition of wines and olive oil
Impedimetric	Gas	Metal oxides (most common is SnO_2 doped with Pt or Pd), operating at ~300–500°C [26, 30] Conductive polymers (doped polypyrrols, polyaniline, polythiophenes, etc.) [31]	Detection of toxic gases and VOC (eg in fire alarm systems), detection of bacterial infections and medical diagnosis, air quality control (eg emissions from industry, agriculture, packaging smells, etc.), food quality control
	Liquid	Conducting polymers [32, 33], conducting polymers modified by ionophores, carbon nanotubes [34]	Determination of alkali metal cations Recognition of taste substances
Acoustic wave (surface acoustic waves, quartz crystal microbalance, etc.)	Gas	Chromatographic stationary phases and polymers, polymer films of phtalocyanines, cyclodextrins, organometallic compounds [35, 36]	VOC detection, air quality monitoring, food quality control
	Liquid	36° *YX* $LiTaO_3$ substrate without chemical coatings [37]	Recognition of taste substances
Optical	Gas	Fluorescent dyes [38, 39], metalloporphyrines [40]	VOC detection (ie toluene, ethanol, methanol, acetone, etc.)
	Liquid	Fluorescent dyes, antibodies, aptamers [41, 42]	Proteins' detection, medical diagnosis
Field effect transistors (FET)	Gas	MOSFET (FET with catalytic metal gate: Pt, Pd, etc.) [43, 44]	Detection of toxic gases and VOC, food quality control (often used together with metal oxide sensors)
	Liquid	ISFET (FET with gate covered by sensitive layer, e.g., plasticized polymers doped by ionophores) [45]	Recognition and classification of foodstuffs

electronic noses and tongues were applied for a number of analytical tasks including analysis of fermentation media and monitoring of biotechnological processes, which are discussed below.

Application of the electronic tongue and noses to the fermentation processes' monitoring

Monitoring of the biotechnological processes is one of the promising tasks for the multisensor systems for the following reasons. Composition of the fermentation media is often well defined and concentrations of the parameters to be measured are often correlated. This allows in some cases using a sensor system as a "software sensor" [49–52]. This means that the values of variables which are difficult to measure, are predicted using secondary measurements that are simpler and/or cheaper to perform and certain mathematical algorithm. Simple information that media composition is deviating from the norm is often sufficient for the process control purposes. Multisensor systems share with discrete sensors the same advantages and drawbacks associated with their application to the fermentation monitoring. On the one hand, rapid, non-expensive measurements allowing real-time follow-up of the process are possible. On the other, contamination of the sensing elements, temporal drift and calibration stability are common obstacles. However, one of the main problems hindering practical use of discrete sensors, namely insufficient selectivity in complex media, is usually solved by using multisensor systems.

It is worth mentioning differences between the electronic tongues and noses when used for this type of analysis. An evident advantage of the electronic noses is that measurements are made in the head space that is without direct contact of the sensors with broths. As a result the contamination of the sensors' surface by the broth components is reduced and possible problems with sterilization and sampling are avoided. The downside of it is that redistribution between liquid and gas phases takes certain time for some compounds especially for the ones present in liquid at low concentrations, which leads to a time lag between changes in the fermented medium and sensor system response [53]. Other problems with gas sensor system include sensitivity to water vapors, which are abundant in the headspace and interfere with sensors' response to the substances of interests. Also, the electronic noses usually provide only for the semi-quantitative analysis. Electronic tongues are capable of performing quantitative analysis of the media and less prone to drift and interferences. However, contamination of sensor surface, the necessity of sterilization if a system is used on-line and adequate sampling of the broth if a systems is used at-line are important issues that need to be addressed. It also worth mentioning that quite often liquid and gas sensors employed in the electronic tongues and noses correspondingly display sensitivity to the different classes of substances. Therefore, as in many other applications the choice of the appropriate system depends on the task and on the key compounds to be detected.

Only very few works on the application of the sensor systems to the monitoring of the anaerobic digestion can be found in the literature. Therefore, we considered useful to start with a review of the applications of the electronic noses and tongues to the other types of the fermentation processes, since such applications are more numerous. Considering that general approach to the measurements and data processing do not vary significantly from the one type of fermentation to the other and analyzed components are often the same, such information may be of interest to the reader.

An electronic tongue consisting of 21 potentiometric chemical sensors with plasticized polymeric membranes was used for off-line measurements of rapid *Escherichia coli* fermentation [54]. The system was capable of measuring concentrations of acetate and ammonia and predicting biomass dry weight with good precision. The same electronic tongue system was applied to the analysis of the model solutions with compositions typical for the *Aspergillus niger* fermentation [55]. Concentrations of ammonia, oxalic and citric acids were measured using the system. Since the electronic tongue was sensitive to the main components changing during fermentation process, it was possible to derive from the sensor system output another practically important process parameter, namely the time elapsed from the start of the growth.

Multi-analyser system consisting of electronic nose (10 MOSFET, 19 MOS comprising. 18 SnO_2 sensors and CO_2 sensor) and NIR spectrometer was employed for the monitoring of the recombinant *E. coli* fed-batch process for tryptophan production [56] and yogurt fermentation [57]. Reference measurements were carried out using mass-spectrometry, standard probes (pH, O_2 and temperature) and HPLC for the determination of sugars and organic acids. Analogous electronic nose system was used for follow-up of the baker's yeasts [58, 59] and recombinant *E. coli* [60] cultivation processes. It was possible to infer from the sensor array output such process variables as cell mass dry weight, ethanol content, and specific growth rate as well as follow the fermentation process. Evidently, the system was not able to measure directly cell mass dry weight and was functioning in this case as a "software sensor". Calibration model for the prediction of this parameter was made using back-propagation neural network. Principal component analysis was employed for the identification of the process state. Due to the problems with drift and calibration stability of the electronic nose used in these studies, it was suggested later on by the same authors [61] to use the system for semi-quantitative analysis of the broths. It was found that semi-quantitative approach allowed monitoring the physiological state of the process while avoiding problems of drift compensation and re-calibration of the array. A commercial electronic nose equipped with 12 sensors with polypyrrol-based conducting polymers sensing elements was applied to the solving problems in biotechnological production of proteins and antibiotics [62]. The electronic nose was capable of distinguishing lot-to-lot variations in medium ingredients quality (casein hydrolisate) and various growth phases during antibiotics bioproduction process and detecting the contamination of the growth media with foreign microorganisms.

Multisensor systems were evaluated as a tool for the process monitoring of the production of fermented foodstuffs. A taste sensor comprising eight potentiometric chemical sensors with plasticized PVC membranes could follow changes of the titratable acidity during the fermentation of the kimchi, cabbage based traditional Korean dish [63]. A taste sensor also based on eight potentiometric chemical sensors with plasticized PVC membranes was used for the fermentation monitoring of miso—traditional Japanese soybean paste [64]. The system was capable of following changes in the miso composition occurring during its fermentation and storage and ripening. Also a correlation was observed between sensors' output and such parameters as titratable acidity and total amino acids' content. An electronic tongue comprising 30 potentiometric chemical sensors with plasticized polymer membranes was used for the follow-up of the fermentation of the cheese starter culture [65]. Early detection of the process deviations from the normal operation conditions could be done using the electronic tongue. Also a good correlation was observed between the sensor systems output and concentrations of organic acids (citric, lactic and orotic) and peptide profile, HPLC measurements being used as reference data for the calibration. Fermentation of the Tokaj wines was monitored using array of six gas SnO_2 sensors [66]. The first PC extracted from the sensor array output correlated with the main parameters changing during fermentation and the sensory quality of the final wine. An electronic nose based on the 32 conducting polymer sensors was applied to the follow-up of the muscatel wine fermentation [67]. Direct measurements of the headspace vapors using electronic nose allowed detecting only changes of ethanol concentration because ethanol was present in high concentrations in the headspace and all sensors of electronic nose displayed sensitivity towards it. Selective sample pre-enrichment using pervaporation technique was employed to remove ethanol from the sample and enrich it with flavor compounds at the same time. Sample pre-treatment allowed following the evaluation of aroma profile of muscatel must during fermentation.

The capability of the multisensor systems to measure metabolites of various microorganisms was evaluated in several studies. The aim of these studies was consequent application of such systems to the detection of microbial contamination and/or discrimination of the microorganisms. A series of studies was done on the discrimination and growth monitoring of various molds and yeast species in the model malt extract medium. Two types of the electronic tongues were used for this purpose. An electronic tongue based on the pulsed voltammetry and consisting of noble metal electrodes [68–70] and both voltammetric and potentiometric electronic tongues [71]. Different species of molds, yeasts and bacteria were could be discriminated. Reference measurements were run using GC and HPLC with electrochemical detection and a good correlation was observed between voltammetric electronic tongue output and concentrations of ergosterol [69] and red-ox compounds [70] that are changing during molds' growth. An electronic nose comprising 16 sensors based on the conducting polymers was employed to measuring volatile compounds produced from the plate cultures [72]. Microorganisms were 12 bacteria and one pathogenic yeast species, which were successfully discriminated by the electronic nose. The application of a multilayer perceptron neural classifier combined with the multi-dimensional parameter extraction from the transient sensors' response was demonstrated to be very successful.

Application of the electronic tongues and noses to the monitoring biogas production processes

Very few attempts were made to use sensor systems for the monitoring of biogas production processes. One of the reasons for it may be more complex and less reproducible composition of the bioreactor feed compared to the other types of fermentations resulting from the variations of the raw materials coming from a number of sources to the plant. Complex and concentrated bioreactor content may aggravate problems with contamination of the sensors and some sample preparation steps may be required. Representative sampling is also an important issue since content of big reactor tanks may be inhomogeneous due to the stagnation zones existing inside it. Therefore, the choice of sampling points or placing of the measuring device becomes very important. Only two works were found in the literature on the application of the multisensor systems to the monitoring of the anaerobic digestion.

An electronic tongue comprising 12 potentiometric chemical sensors was applied to the analysis of the biomass samples collected at the biogas plant [73]. All samples were analyzed using conventional analytical techniques and these data were consequently used for the electronic tongue calibration. Minimum sample preparation was employed, which consisted in rough filtration of sample with the aim to separate suspended solids and fibers and followed by the sample 10-fold dilution. It was found that sensor system could determine concentration of such parameters as nitrate, ammonia, copper, zinc as well as chemical oxygen demand and total volatile fatty acids.

An electronic nose consisting of MOSFET and MOS gas sensors and NIR spectroscopy combined with multivariate calibration (PLS-regression) was evaluated as a tool for anaerobic digestion monitoring [12]. A bioreactor was fed with a mixture of cellulose, albumin and minerals and exposed to an overload of glucose. It was demonstrated that electronic nose could follow changes in methane and acetate concentrations while NIR could predict microbial biomass and total volatile fatty acids and acetate content.

Conclusions

Biomimetic sensor systems, electronic tongues and noses, represent a novel approach to the application of chemical sensors combining a biologically inspired architecture with latest achievements in the sensor science itself. Electronic tongues and noses are of particular interest for the analysis of complex liquids and gas mixtures correspondingly. They possess all the advantages of the chemical sensors such as rapid measurements, possibility of easy automation of the sensor set up and relatively simple and inexpensive instrumentation. At the same time the use of systems instead of discrete sensors allows dealing successfully with such traditional problem of the discrete sensors as insufficient selectivity in the multicomponent media.

Electronic tongues and noses offer the possibility to perform recognition and classification and quantitative determination of components' concentrations simultaneously in multicomponent media. This feature makes multisensor systems a promising tool for the processes follow-up, when the content of some components can be measured quantitatively and, at the same time, the state of the process and its correspondence to the normal operation conditions can be assessed. Numerous successful applications of the multisensor systems in food, environmental and industrial analysis were reported in the literature during the last decade. Multisensor systems have also demonstrated good potential as a process monitoring tool for biotechnological processes. Despite that, applications of the electronic tongues and noses for the follow-up of biogas production processes remain scarce up to date, which is presumably due to a more complex and less reproducible composition of the biomass compared to other fermentation media. Evidently, such important practical issues as sensor surface contamination in complex media, drift of characteristics on certain occasions and stability and reproducibility of the calibrations should be addressed to make sensor systems widely applicable for routine analysis. However, we believe that wider use of the multisensor systems as process analytical tool in the biotechnological industry including biogas production is just a question of time.

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