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The monitoring of methane fermentation in sequencing batch bioreactor with flow-through array of miniaturized solid state electrodes

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ABSTRACT

Electronic tongues (ETs) based on potentiometric sensor arrays are often used for foodstuff classification, origin recognition, estimation of complex samples' properties, etc. In the last few years they were also applied for various fermentation monitoring, such as *Aspergillus niger* fermentation, light cheese production, batch *Escherichia coli* fermentation, as a devices capable of fast, inexpensive, automated and on-line control of the process. In this work a novel application for ET is proposed—flow-through array of solid state electrodes was used for the analysis of samples obtained during methane fermentation (anaerobic digestion) of whey in sequencing batch bioreactor, according to their volatile fatty acid (VFA) content and chemical oxygen demand (COD).

1. Introduction

Methane fermentation, also known as anaerobic digestion, is a biotechnological process, during which waste is transformed by microorganisms under anaerobic conditions and valuable biogas is produced. Process itself, its duration and the quantity of biogas achieved depend on the raw material and bacteria used as inoculum, i.e. mixed population of microorganisms. In this process, raw material is at first converted to mono- and oligomers, such as aminoacids, long chain fatty acids, saccharides, and so on. The next stage leads mainly to the production of volatile fatty acids (VFAs) and acetic acid followed by gases (H_2, CO_2), which are finally transformed to methane and CO_2. During the fermentation also the concentration of simple ions and pH varies. Moreover, there are many factors that can disturb the process itself, or slower it [1,2]. The complex microbial population responsible for biogas production exists in a dynamic equilibrium. This state is sensitive to many chemical and physical factors. An increase in volatile fatty acids, for example, and decrease in the pH of bulk solution, subsequently inhibits the methanogensis step and leads to process failure. The interdependence of the different microbial groups involved in anaerobic digestion is the main cause of the process instability.

The concentrations of both gaseous and liquid components taking part in the fermentation are nonlinearly dependent, and there are various approaches to model that process [3,4]. Therefore, there is a need to monitor fermentation not only by pH measurement or biogas analysis, but also by more detailed observation of liquid phase in the bioreactor. Complexity of the samples originating from anaerobic digestion process is very high, and usually single factors such as methane content of biogas or, e.g. fatty acids content of liquid phase is not sufficient for full characterization of actual stage of the process. However, the complex image of whole process can be obtained with the use of sensor array equipped with chemical sensors of various selectivity (so-called electronic tongue, ET).

Electronic tongues are devices that combine sensor arrays with various statistical and pattern recognition tools in order to perform complex characterization of samples [5]. Till now, such devices were proposed for various fermentation process monitoring [6–9]. A potentiometric electrode array formed by 8 cross-sensitive sensors and pH electrode was applied to the analysis of simulated solutions typical for *Aspergillus niger* fermentation process. The proposed system was capable of simultaneous determination of ammonium, citrate and oxalate in complex media with good precision, even in the presence of sodium azide (suppressor of microbial activity used in fermentation media [7]). Similar system, composed of 30 electrodes, was applied in the monitoring of batch fermentation in light cheese production. It was showed, that it allows for discrimination of samples from fermentation batches run under "abnormal" and "normal" operating conditions at early stage of fer-

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mentation. Also it was possible to determine organic acids (citric, lactic and orotic) present in the fermentation media [8]. Another example of ET application to fermentation monitoring is the estimation of changes in the media composition, determination of organic acids, and correlation with biomass increase in *Escherichia coli* fermentation [9].

In this work solid state electrode (SSE) array working in flow conditions is proposed as an ET device capable of estimation of fermentation conditions during anaerobic digestion. Flow-through mode of measurements allows for on-line process control, whereas modular architecture of the array is advantageous for convenient construction, calibration, and selection of sensors. SSE array signals were measured in samples that were gathered from 48 h methane fermentation process carried out in sequencing batch bioreactor, with whey as the main resource.

2. Experimental

2.1. Methane fermentation

Fig. 1 shows the experimental set-up of anaerobic digestion process used in this study. The set up consisted of a column bioreactor of 13, 1 l working volume, equipped with temperature regulation, and water displace system for biogas collecting. Bioreactor worked at mesophilic conditions (35 ± 1 °C), as an anaerobic sequencing batch reactor. Every 48 h reactor was fed with 500 ml of substrate, after which the same volume of effluent has been drained. Reactor load was 1.3 g COD dm^{-3} day^{-1} and apparent flow was 0.25 l day^{-1}. The acid whey used in this study as a substrate to anaerobic digestion was obtained from O.S.M.Błonie (dairy near Warsaw, Poland). The whey samples were drained from whey container and collected in 5 l tanks, transported to laboratory and stored at temperature 4 °C. The whey characteristic was: COD = 70.2 g dm^{-3}, pH 3,5, DM = 5.87 g DM g (dry matter content). Samples were gathered after 24 and 48 h after the feeding.

2.2. Sample preparation and characteristics

Samples were taken to determine pH, COD and VFA concentrations (50 cm^3 after 24th hour of the cycle and 450 cm^3 after 48 h at the end of the cycle). Supernatant from biomass separation (centrifugation: 20 min, 5000 rpm) was used for all chemical determinations. COD was determined according to standard methods. VFA concentration was determined using Macherey-Nagel Nanocolor LKT 3000 test tubes (method no. 0-50). The volume of biogas produced and its composition were measured every 24 h (biogas analyzer GA 45 Geotechnical Instruments, Fig. 2).

2.3. Preparation of chemosensitive membranes

For all experiments redistilled water and chemicals of analytical-reagent grade were used. The membrane components were supplied by Fluka: ionophore X (sodium ionophore X, 4-tert-butylcalix[4]arene-tetraacetic acid tetraethyl ester), valinomycin (potassium ionophore I), TDDA (hydrogen ionophore I, tridodecylamine), KTFPB (potassium tetrakis [3,5-bis(trifluoromethyl)phenyl] borate), KTPClPB (potassium tetrakis(4-chlorophenyl)borate), TDMAC (tridodecylmethylammonium chloride), DOS (bis(2-ethylhexyl)sebacate), o-NPOE (2-nitrophenyl octyl ether), PVC (poly(vinyl chloride)). The ionophore dichloro(5,10,15,20-tetraphenylporphyrinato)zirconium(IV) (Zr(IV)[TPP]Cl$_2$) was synthesized via a metallation of the free porphyrin (Porphyrin Products) using ZrCl4 (Fluka) [10].

Chemosensitive layers contained appropriate ionophores (~1.0–2.0 wt.%), 20–50 mol% versus ionophore lipophilic salt, 61 wt.% plasticizer, and 31–33 wt.% poly(vinyl chloride). Membrane components (100 mg in total) were dissolved in 0.5 ml of tetrahydrofuran and this solution was deposited on the surfaces of solid state planar electrodes, cleaned thoroughly with distilled water and methanol.

After membrane solvent evaporation, the sensor array was conditioned for 24 h. All EMF measurements were carried out with double junction Ag/AgCl electrode as reference electrode, using a potentiometric multiplexer (EMF 16 Interface, Lawson Labs Inc., Malvern, USA).

2.4. Sensor array

Potentiometric sensor array was build using solid state electrodes (SSEs) with various types of PVC membranes doped with electroactive components [11–13]. Miniaturized SSEs were fabricated using PCB technology and equipped with chemosensitive membranes selective towards acetic acid and other VFA anions (AC), lipophilic cations (CS), lipophilic anions (AS), H$^+$ ions, K$^+$ ions, Na$^+$ ions (detailed compositions of the membranes can be found

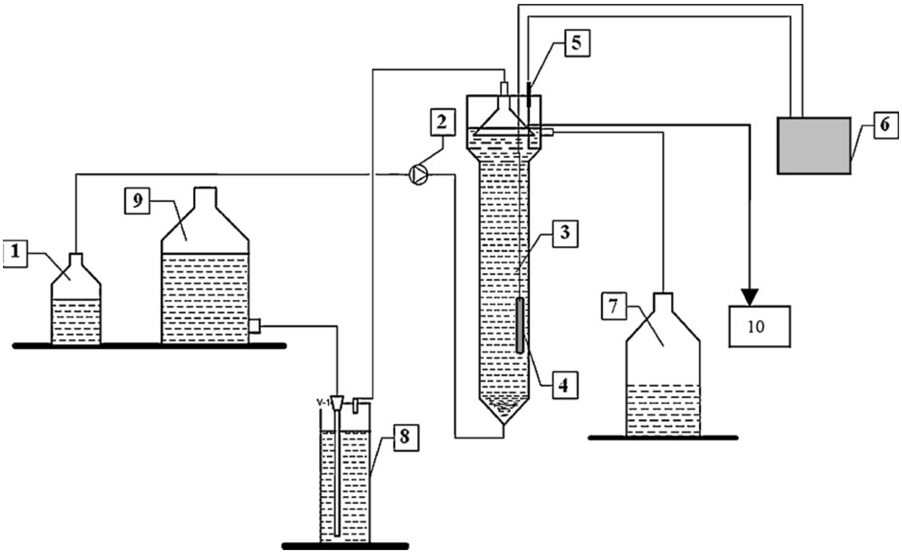

Fig. 1. Methane fermentation set-up: 1—substrate container; 2—peristaltic pump; 3—column bioreactor; 4—heater; 5—temperature sensor; 6—temperature regulator; 7—effluent container, 8 and 9—water displace system for biogas collecting, 10—sampling of liquid phase

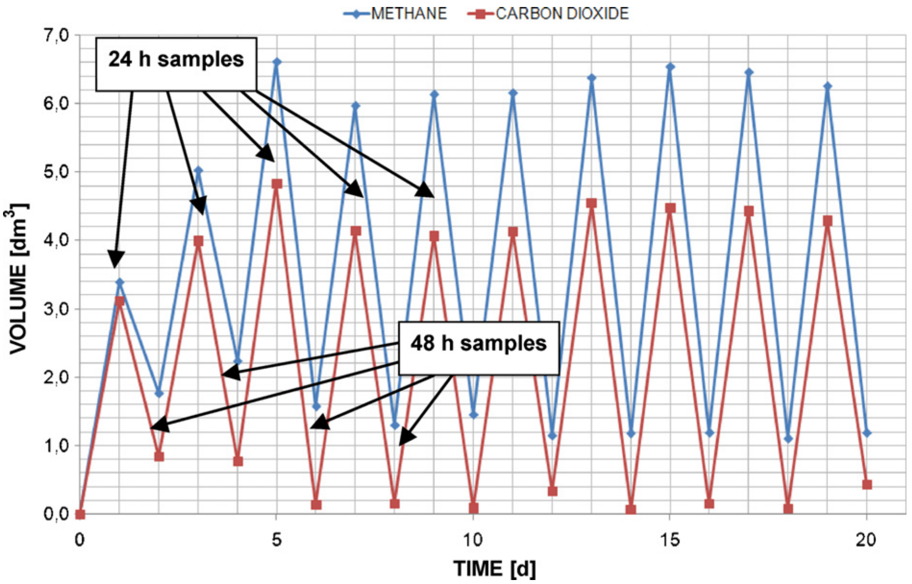

Fig. 2. Daily methane and carbon dioxide production.

in [11–13]). AC membranes contained 1.04 wt.% Zr(IV)[TPP]Cl_2, 1.10 wt.% KTFPB, 65.70 wt.% DOS, 33.26 wt.% PVC.

The modular flow-cell system (the design of which is a subject of polish patent application [14], housings are commercially available in transparent and black version) has been developed by MEDBRYT, Warsaw, in the framework of FP6 WARMER programme (Project FP6-034472, WAter Risk Management in EuRope). The main element of flow-through system is a housing for sensor, presented in Fig. 3. It is provided with two arms, enabling horizontal connection with other housings—or with flow-input/output pieces, sticked always to the ends of set. Each element has a specially designed hollow for gasket, so that liquid-flow channel is formed and the risk of leakage between two elements is minimized. Flow-input and flow-output pieces are also drilled in order to enable mounting the whole set of housings to a flat, stiff surface (e.g. internal construction of measuring unit). While locking sensor, one more element has to be used—a pill-shaped electrical connector, inserted into the mount-piece. Thanks to the 2-pin output of the connector, electrical signal generated by sensor can be transmitted to the analytical unit.

A set of modules can be connected into a measurement loop-flow by use of standard nut and ferrule connectors (28-1/4" threads). All parts of the flow-cell system are made of ABS (Acrylonitryl-Butadien-Styren), which is very suitable material for use in water measurement. Each element of the system can be connected and disconnected fast and easy, causing no risk of physical damaging sensors nor reference electrode.

Flow-through cell was constructed on the basis of 11 single modules to be connected with each other (Fig. 3). Sample was transported using peristaltic pump to a flow system (Fig. 3). System contained 10 solid state electrodes (2 SSEs of AC, CS, AS and H^+ type, and 1 SSE of K^+ and Na^+ type) and a reference electrode, every one of them located in a separate module. Electrodes were connected to a multiplexer that passed the amplified signal to a computer. All data analysis was performed in MatLab (The MathWorks Inc., Natick, USA) and Origin (Microcal Software Inc., Northampton, USA) software.

3. Results and discussion

Electronic tongue developed at Warsaw University of Technology consists of potentiometric sensors which selectivities can be controlled and strictly designed [12,13,15]. It uses various transducers, such as macro-electrodes, solid state miniaturized electrodes, working both in static and flow conditions [13,15]. The chemosensitive membranes' compositions is the main factor determining the recognition capabilities of ET in a particular case. For previous application of ET systems, such as the recognition of various foodstuffs [12], classification of plant homogenates [16],

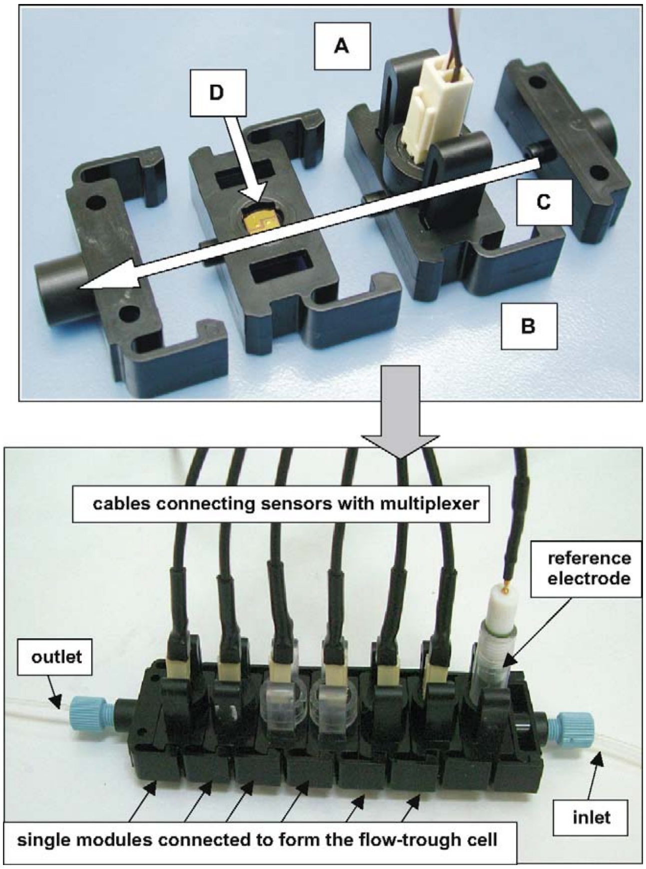

Fig. 3. Flow-trough cell for sensor array measurements: A—plug; B—sensor compartment with a channel (C); D—cavity for sensor placement with SSE. The design of modular flow-cell system is a subject of polish patent application [14].

Table 1
Characteristics of the methane fermentation samples.

Number of samples	Samples gathered after		pH		Volatile fatty acids (VFAs) n_{CH_3COOH}/mmol dm^{-3}		Chemical oxygen demand (COD)/mg O$_2$ dm^{-3}	
	48 h	24 h	pH > 7.9	pH < 7.9	$n > 2.0$	$n < 2.0$	COD > 700	COD < 700
			H-pH	L-pH	H-VFA	L-VFA	H-COD	L-COD
90	■		■		■		■	
90	■			■	■		■	
90	■			■	■		■	
30		■	■		■			■
30		■	■			■		■
30		■	■		■		■	
30		■		■		■		■

determination of urea and creatyninine in dialysate fluids [17], monitoring of cell cultures [18], fusion of selective and partially selective sensors was proposed. In most of the applications electrodes of general lipophilic anion- and cation-selectivity (AS and CS type) played a crucial role, since they were able of organic ions sensing. However, for methane fermentation monitoring there was a need to apply a receptor capable of comlexation of carboxylic acid anions (mainly acetic acid anions), in order to enhance the information linked with the fermentation process run.

Metalloporphyrins are a class of anion ionophores that have proven to be useful in the preparation of potentiometric sensors with various selectivity patterns. It has been shown that the selectivity of metalloporphyrin–anion interaction depends mainly on the metal cation present in the ionophore structure [19,20]. Besides the varying selectivity, the advantages of metalloporphyrins include high stability, sufficient lipophilicity and the possibility of the modifications of porphyrin ring to introduce steric or electron effects [21]. The chemical grafting of metalloporphyrin to the polymeric membrane matrix is also possible [22].

Zr(IV)–porphyrins was first introduced as fluoride-selective ionophores [10,23]. Recently, Zr(IV)–porphyrins has been used also as acetate-selective ionophore for construction of sensors in flow-injection analysis enzymatic system designed for acetylcholine detection [24]. It should be noted that there is very few acetate-selective ionophores described in the literature. Only (a,a,a,a)-5,10,15,20-tetrakis[2-(4-fluorophenylureylene)phenyl]-porphyrin has been reported earlier as acetate-selective ionophore. However, the selectivity of this compound was rather poor, as its interaction with analyte ion relies on hydrogen bonds.

As Zr(IV)–porphyrin is the only useful acetate-selective ionophore described to date, it was chosen for the construction of SSE for electronic tongue system designed to recognize samples from methane fermentation, which contain varying amounts of acetic acid. Although super-nernstian behavior of the sensors was noticed (slopes higher than theoretical 59 mV/dec, i.e. 65–74 mV/dec), the responses of the electrodes were fast and accurate.

The long-term stability of the SSEs was investigated during 3 months in the flow-through automated measuring system. The obtained calibration curves were repeatable in time. Only small variations or slight decrease of the slope values and mean values of selectivity coefficients have been noticed (e.g. for K^+- and Na^+-selective electrodes following values of slopes were observed during 3 months: 54.3 ± 3.5 mV/pK^+ and 51.5 ± 5 mV/pNa^+).

After the preparation flow-through SSE array was applied to estimate fermentation stage and stability of the anaerobic digestion process. At the beginning of each cycle 500 ml of effluent was drained from the top of the fermentation column and then the reactor was fed from the bottom with 500 ml of substrate, which corresponds to 24.8 g COD. Liquid samples used for electronic tongue testing were taken from the top of the bioreactor during last 8 days of fermentation, when the process was more stable than in the beginning (Fig. 2). Average daily biogas production was 7.6 dm^3 d^{-1} and the average methane content was 63% (see Fig. 2). COD reduction during last 8 days of the fermentation was high and close to 98%.

The results of analysis of the liquid samples taken from the top of the bioreactor (pH, VFA content, COD) which represent composition of the reactor effluent were applied as reference data for ET data analysis. Samples were gathered from 48 h process sequence, after 24 and 48 h after feeding. They were divided into 7 types, according to the time, when they were sampled, and their pH, VFA content, and COD (see Table 1). Samples of pH lower than 7.9 were indicated as low pH samples (L-pH), otherwise as high pH samples (H-pH). The same schema was applied in the case of VFA content—samples containing less then 2 mmol dm^{-3} CH_3COOH were designed as low VFA samples (L-VFA), otherwise as high VFA samples (H-VFA). COD higher then 700 mg O$_2$ dm^{-3} was marked as H-COD, in contrast to L-COD.

As can be seen from Table 1, the 7 types of samples had very differentiated characteristics. Among 48 h samples 3 groups were observed differentiated by pH, VFA content and COD, and among 24 h samples 4 groups were found. Even though some factors were similar, e.g. most of the 24 h samples were H-pH and L-COD (higher pH and low COD are linked with the first phase of fermentation, when small amount of acidic compounds are present in the liquid phase), there were samples that exhibited less typical behavior (i.e. L-pH and H-COD samples). Generally, 48 h samples should exhibit L-pH and H-COD, but this is also not a strict rule (some samples are H-pH and L-COD). That variability was confirmed by various amounts of VFAs observed, measured by means of acetic acid content. That factor is so differentiated in this set of samples, that its high or low values cannot be linked with a particular kind of samples. This is probably caused by the fact, that only the concentration of acetic acid was determined in the samples, whereas also other fatty acids (influencing pH and COD) should be taken into account. Moreover, the variability can be observed also in methane and CO_2 content in gaseous phase (see Fig. 2) Even though the samples were gathered in more stable process conditions than at the beginning, there were still some differences observed in the samples gathered after the same time in each sequence.

The first objective was to differentiate samples gathered after 24 and 48 h of every sequence. Potentiometric signals of the sensor array were measured and sensor array outputs were processed by Partial Least Squares–Discriminant Analysis (PLS-DA). It was found, that the differentiation among various kind samples occurred (Fig. 4). Partial overlapping of the clusters was caused by slight instability of the process, which was confirmed by COD, methane, CO_2, and VFA determination (Fig. 2 and Table 1). Moreover, the liquid samples were taken from the top of the column, whereas the main anaerobic digestion process occurs at the bottom half of the reactor, therefore there is no well-defined difference in COD and

VFA concentrations between some 24 and 48 h samples. On PLS plot (see Fig. 4) 2 clusters are linearly separable. One cluster is formed by 24 h samples that exhibit their “typical” values (i.e. H-pH and L-COD). It was noticed, that the overlapping 24 h samples exhibited similar characteristics to the 48 h samples (L-pH or H-COD), and that is the reason why that set is not so clearly separable from 48 h samples.

Results of the measurements of 24 and 48 h fermented samples are presented in details in Fig. 5. Sensor signals were processes with the use of partial least squares (PLS) analysis with target matrix containing information on samples’ pH, VFA content, and COD. The calibration towards COD values provided satisfactory results (see the correlation coefficient, values of slope and intercept in Fig. 5A), however in the middle range of COD the determination is not very precise. This can be linked with nonlinear dependence between COD and concentrations of ionic components (because COD is determined not directly by the sensors used), moreover, all signals of the electrodes are also nonlinearly dependent on pH. Therefore, we decided to split the dataset into two subsets according to their pH level (H-pH and L-pH samples). The results are presented on the bottom part of Fig. 5B and C. More precise determination was in this way obtained—not only values of intercepts

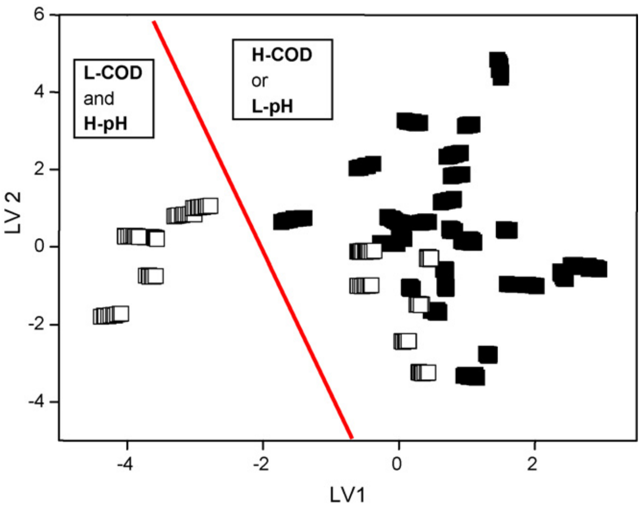

Fig. 4. PLS plot of samples fermented for 24 h (□) and 48 h (■).

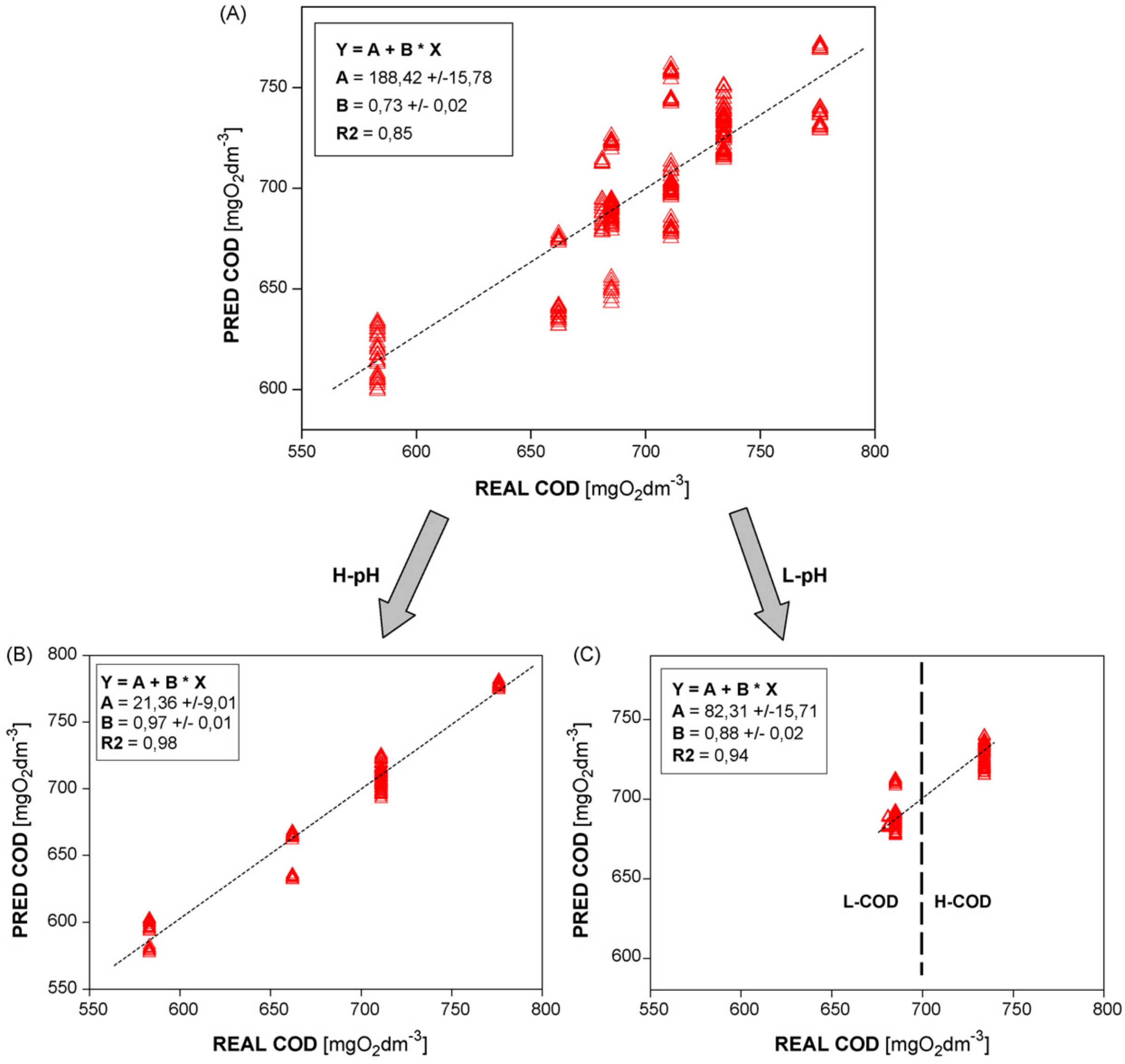

Fig. 5. PLS prediction of chemical oxygen demand (COD) of samples measured.

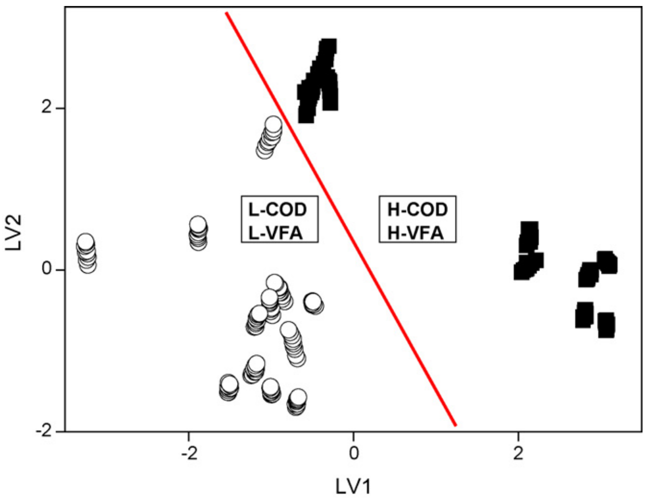

Fig. 6. PLS plot of L-pH samples.

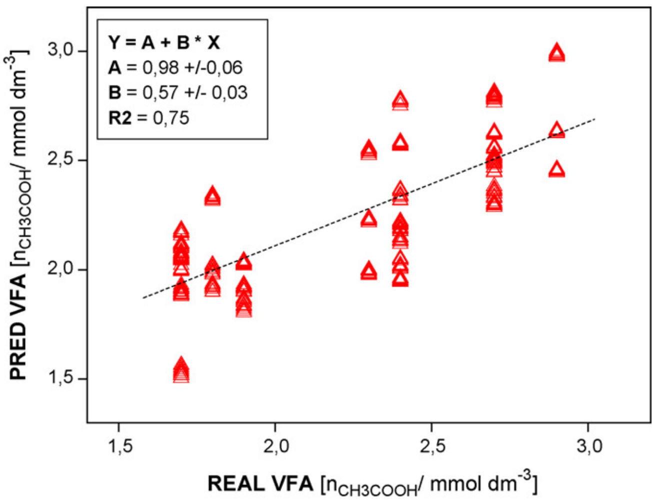

Fig. 7. PLS prediction of volatile fatty acids (VFAs) of samples measured.

were improved (values of slopes closer to 1, values of intercepts closer to 0), but also the correlation coefficient was improved to 0.94–0.98. Even though in Fig. 5C the population of L-COD samples is partially overlapping H-COD samples, they can be linearly separable on PLS scores plot (see Fig. 6).

All samples gathered after 24 and 48 h exhibited VFA at the level of 1.7–2.9 mmol CH_3COOH dm^{-3}. Sensor signals calibrated with the use of PLS in order to predict real value of VFA are presented in Fig. 7. There can be find good correlation between real and predicted values ($R^2 = 0.75$). In order to enhance the precision of the determination, the same schema as previously was proposed—the samples were divided into two subsets, according to their pH. Again, more precise and accurate results were obtained: higher slopes (0.98 ± 0.01 for H-pH samples and 0.88 ± 0.02 for L-pH samples) and higher correlation coefficients (0.99 for H-pH samples and 0.94 for L-pH samples). The better results can be caused also by nonlinear dependence of sensor signals when exposed to various levels of pH (as explained above), moreover, in various pH various number of dissociated molecules of VFAs are present in the solution. Even though precise determination of VFA in L-pH samples is not possible, there is still possibility of differentiation of samples of low and high VFA content on PLS scores plot (see Fig. 6).

4. Summary

The presented results show, that the electronic tongue based on flow-through array of miniaturized solid state electrodes is capable of the monitoring of methane fermentation in sequencing batch bioreactor. As pointed out in [6], till now only few attempts were made to apply sensor arrays, both electronic noses and tongues, to the monitoring of biogas production. The main reason is very complex and poorly reproducible composition of process media in comparison to other fermentations

In this work we wanted to show that ET could be used to estimate stage of fermentation and stability of the process, which can be thrown out of balance by means of some of the compounds present in culture medium. The applied flow-through array allows for on-line process control, and its modular architecture is advantageous when composing sensor set regarding their future applications. Moreover, Zr(IV)–porphyrin was proposed as acetate receptor for electronic tongue applications.

The monitoring preformed by ET measurements of liquid phase lead to satisfactory determination of VFA level and COD, and estimation of fermentation stage. In future works, detailed studies are planned with the use of additional voltammetric sensors for the characterization of redox components of the fermentation liquid phase (e.g. alcohols and carbohydrates), which will be helpful in the development of hybrid ET for fermentation monitoring.

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