Ethanol quantification in pineapple waste by an electrochemical impedance spectroscopy-based system and artificial neural networks

Claudia Conesa[a], Luis Gil-Sánchez[b], Lucía Seguí[a], Pedro Fito[a], Nicolás Laguarda-Miró[b,*]

[a]Instituto de Ingeniería de Alimentos para el Desarrollo (IIAD), Universitat Politècnica de València, Camí de Vera s/n, 46022 Valencia, Spain.

[b]Instituto Interuniversitario de Investigación de Reconocimiento Molecular y Desarrollo Tecnológico (IDM) Universitat Politècnica de València, Universitat de València , Camí de Vera s/n, 46022, Valencia, Spain.

*Corresponding author at: Universitat Politècnica de València, Camí de Vera s/n, 46022 Valencia, Spain. Tel.: +34 963877007; Fax.: +34 963877189, *e-mail address:* nilami@iqn.upv.es (N. Laguarda-Miró)

ABSTRACT: Electrochemical impedance spectroscopy (EIS) technique has been applied to determine the ethanol concentration in pineapple waste samples. To do this, six different concentrations of ethanol were added to the pineapple samples and were analyzed using the system designed by our research group and consisting of the called Advanced Voltammetry, Impedance Spectroscopy & Potentiometry Analyzer (AVISPA) device associated to a stainless steel double needle electrode. Results indicated that phase data in frequencies between 6.0×10^5 Hz and 8.0×10^5 Hz showed the highest sensitivity to ethanol concentrations. A principal component analysis (PCA) confirmed the potential discrimination and partial least squares (PLS) regression showed mathematical models able to quantify ethanol in samples accurately. In order to implement flexible and precise models in programmable equipment, different types of artificial neural networks (ANNs) have been studied: Fuzzy ARTMAP and multi-layer feed-forward (MLFF) algorithms. As a result, a coefficient of determination (R^2) = 0.996 and a root mean square error of prediction (RMSEP) = 0.408 have been obtained. Therefore, it allows us to introduce this technique as an

alternative method for ethanol quantification along the fermentation of pineapple waste in an easy, low-cost, rapid and portable way.

Keywords: Electrochemical impedance spectroscopy; ethanol; pineapple waste; artificial neural networks.

1. Introduction

Global energy demand is significantly increasing due to global population growth and the industrialization of the emerging countries [1]. The depletion of fossil energy resources and the emission of pollutants into the atmosphere [2] have led to the rise of new energy policies promoting renewable energies, such as bioethanol [3].

In this scenario, second-generation bioethanol, which is produced from the fermentation of lignocellulosic biomass such as agricultural, forestry or industrial wastes, deserves special attention. Unlike first generation bioethanol (obtained from sugar or starch-rich crops) second-generation of this biofuel helps to diversify energy supplies without competing in the global food market [4, 5]. Furthermore, the use of waste as a source for bioethanol production would also add up value to the whole manufacturing process. This biofuel can be used singly, as an additive replacing methyl tert-butyl ether (MTBE), or can be used in mixtures with conventional gasoline in a variable percentage from 10% to 85% [6, 7, 8]. As a result, bioethanol is the most widely used biofuel in the transport sector [9]. Nowadays, pineapple industrial waste is considered as a potential bioethanol source because of its high content of fermentable sugars and highly hydrolysable cellulose and hemicellulose [10, 11, 12]. This waste represents up to 50% (w/w) of the total processed fruit whose world production has reached 24 millions of tons in 2014 [13].

Hydrolysis, fermentation, distillation and dehydration are the necessary steps for bioethanol production from lignocellulosic biomass [14]. In the specific case of the fermentation step, performance depends on the operating conditions (pH, oxygen content and temperature), the raw material properties (initial fermentable sugars content) and the used microorganisms (yeast strain and the viability of cell populations) [15]. Therefore, a proper monitoring of the process is of capital importance. To date, chromatographic and enzymatic methods are highlighted among the current techniques to determine ethanol content.

Chromatographic methods such as gas-chromatography (G-C) and high-performance liquid chromatography (HPLC) are accurate and considered as a reference but they are time-consuming and complex pretreatments are needed (distillation, pervaporation) [16]. On the other hand, enzymatic methods are easier although spectrophotometric techniques are generally required to follow the enzyme-catalyzed reactions. As a consequence, they are undesirable for complex media due to the presence of interfering substances [17]. In contrast, electrochemical methodologies are emerging as an alternative to the traditional ones in order to identify chemical compounds in an easy, fast, non-destructive and on-line way. Specifically, electrochemical impedance spectroscopy (EIS) is one of the most remarkable ones. It consists in analyzing properties of the samples by means of electric alternating signals (current or voltage) at different frequencies and measuring the corresponding electric response (voltage or current) within an electrochemical cell [18, 19].

In previous studies, identifying and quantifying fermentable sugars in pineapple waste as well as monitoring its enzymatic saccharification has been possible by using a device called Advanced Voltammetry, Impedance Spectroscopy & Potentiometry Analyzer (AVISPA) that combines EIS with a double needle stainless steel sensor [20, 21]. Furthermore, it has been necessary to use artificial neural networks (ANNs) for a proper statistical treatment of the EIS data. ANNs are mapping structures simulating the neural system of the human brain. These structures are able to solve problems involving complex and non-linear data even in case of imprecise and noisy data sets. Among the different ANNs, Fuzzy ARTMAP and multi-layer feed-forward (MLFF) algorithms are able to be implemented in portable equipment [22]. These algorithms are characterized by a high accuracy, fast calculation, ease to use and low memory requirements that facilitate their application in programmable components such as microcontrollers, Digital Signal Processors (DSP) or Field Programmable Gate Arrays (FPGA).

Consequently, the aim of the present study was to validate the designed EIS-based system to quantify added ethanol in real pineapple waste samples and create reliable ANNs-based models able to be implemented into programmable devices.

2. Material and methods

2.1. Electrochemical impedance spectroscopy equipment

The EIS measuring system has been designed by the Group of Electronic Development and Printed Sensors (GED+PS) belonging to the Instituto Interuniversitario de Investigación de Reconocimiento Molecular y Desarrollo Tecnológico (IDM) at the Universitat Politècnica de València (UPV). It consists of three parts: the AVISPA device, the sensor and the specific software. The AVISPA device is able to run tests for potentiometry, pulse and cyclic voltammetry and impedance spectroscopy. It includes a Field Programmable Gate Array (FPGA), a 12-bit Digital-to-Analog Converter (DAC), two 12-bit Analog-to-Digital Converters (ADC) and different analog blocks [20]. The software application was developed using Visual Basic® 6.0 (Microsoft, Redmond, WA, USA) to be run in a PC. It includes a section for EIS that allows the selection of the frequency sweep (from 0.01 Hz to 10 MHz), the current scale (up to 32 current scales) and the amplitude of the variable sinusoidal voltage signals (amplitude up to 1 Vpp). Finally, a double needle electrode (working and counter electrodes) made of stainless steel was designed. The needles dimensions were 1.5 cm long and 1 mm in diameter and they were separated by 1 cm in order to create a stable electric field.

2.2.Laboratory analyses

Pineapple fruits (*Ananas comosus* L. cv. “MD-2”) were selected avoiding external defects. Once the fruits were washed in a NaClO (0.1%) solution and the pulp and the crown were removed, peel and core (waste) were mashed in a blender (Avance Collection Blender HR2097/00 800W, Philips, Amsterdam, The Netherlands). Finally, the pH was adjusted to 5 by adding NaOH 1N (Panreac Química, S.L.U., Barcelona, Spain). The use of the same raw material along the laboratory analyses prevented any effect of potential interfering compounds in the laboratory analyses.

Preliminary assays in this research line established the expected ethanol concentrations after alcoholic fermentation of pineapple waste [23]. Attending to these results, EIS measures were conducted to ethanol (purity = 96%, Panreac-Química, S.L.U.) dissolved in pineapple waste at six different concentrations: 0% v/v (0 g/l), 2.5% v/v (19.725 g/l), 5% v/v (39.45 g/l), 7.5% v/v (59.175 g/l), 10% v/v (78.9 g/l) and 20% v/v (157.8 g/l). Analyses were conducted in triplicate at 25 ºC in a thermostatic bath (PolyScience®, Niles, IL, USA). Consequently, a total of 54 EIS measurements (6 x 3 x 3) were performed.

Once the sensor was completely introduced into each sample, the AVISPA device applied sinusoidal signals at 100 different frequencies (between 1 and 10^6 Hz). Then, the electronic device sent the data to the PC and the software program calculated the modulus and phase values for each frequency. Finally, the corresponding plots were generated.

2.3.Multivariate analyses of data

Specific multivariate analyses, such as principal component analysis (PCA) and partial least squares analysis (PLS), have been successfully applied to process complex data sets obtained using EIS techniques [24]. The SOLO© software program (Eigenvector Research, Inc., Manson, WA. USA) was used for these analyses. Specifically, PCA was conducted to reduce dimensionality of data variables and to detect structures in the relationships between variables [25]and PLS analysis was performed in order to find a robust linear relationship between two matrices, X (the obtained EIS measurements) and Y (the added ethanol concentrations) and check its statistical validity [26, 27]. Finally, the coefficient of determination (R^2) and the root mean square error of prediction (RMSEP) are used to test the predictive significance of the obtained PLS-models as they are reference parameters for this purpose [26].

2.4.Training the Fuzzy ARTMAP neural network

Fuzzy ARTMAP networks use the so-called adaptive resonance theory (ART) and it is based on the use of prior actions to predict subsequent steps [28, 29]. The method of operation is based on finding similarity between the input data and those previously classified. If similarity is found, the network associates the input data to the corresponding previously established category and if not, a new output category is created for this data. The element determining similarity between input data and those previously existing is a vigilance parameter called ρ. On the other hand, another parameter called learning parameter (β) determines the learning rate of the network when new data are introduced as well as the robustness of the model. Fuzzy ARTMAP can be used to create supervised classification systems by using 66% of the data for the training phase and the remaining 33% of the data for the test phase. A diferencia de la red MLFF, en este tipo de red no se utiliza la fase verificación, con la fase de entrenamiento la red queda plenamente configurada y, posteriormente, se realiza el test de la red neuronal utilizando datos que no han participado en la fase previa de entrenamiento. The relationship between output nodes from both networks is performed by a specific module called mapfield connection. The module is a memory register whose data vary and increase as new data are incorporated.

Fuzzy ARTMAP networks have been used in many applications such as electronic nose systems [30, 31] and electronic tongues [32, 33], showing good and reliable results even with a limited number of samples [34]. Despite their wide range of successful uses, algorithms can be complex and may present difficulties on computer applications particularly if there is a memory restriction. In most cases, the algorithm is implemented on a PC and the memory is usually large enough for the algorithm to work properly. The problem may arise when the Fuzzy ARTMAP is implemented on portable devices using low-cost microcontrollers with a limited memory. In these cases, low memory demand algorithms are needed.

In order to satisfy this requirement, Simplified Fuzzy ARTMAP (SFAM) was developed achieving lower computational requirements and easier network architectures [35]. This simplified network was used by Garrett [36] to develop a MATLAB (MathWorks, Natick, MA, USA) toolbox. Using this toolbox functions, our research group has developed a specific MATLAB® graphical user interface. This application is focused on optimizing the algorithm by both getting the best classification rate and the minimum mapfield size [37]. Thus, we can achieve an accurate classification with low memory requirements. The designed application scans ρ and β parameters in a value range and steps that can be set by the user. For each combination of ρ and β, the application determines the mapfield size and the classification rate so that the optimal values for ρ and β can be selected. In this way, the memory requirements can be controlled as they are directly related to the amount of data for the training phase. This application has been successfully used in several food classifications [38].

2.5.Training the MLFF neural network

MLFF algorithm is one of the most popular ANN and it has been applied to a wide range of chemistry-related problems [39]. MLFF consists of neurons that are arranged into layers. The first one is called the input layer, the last one is called output layer, and those between them are the hidden layers. Moreover, each neuron in a particular layer is connected with all neurons in the next one. MLFF algorithms always require a training stage, where the weights of each neuron are set and reflect the degree of importance of the given connection, followed by a validation step [40].

In the present work, the commercial ANN software program Alyuda Neurointelligence 2.2© (Alyuda Research Inc., Los Altos, CA, USA) was used to design the MLFF. First, the experimental data was randomly divided into three sets: training (70%), that build model weights and bias of the neurons; validation (15%), used for tuning the parameters of the model; and test (15%) for check the network with new data that have not participated in the training and validation tasks. This random division of data is done by the software program itself [41, 22]. Cross validation, early stopping in the training phase and a proportional number of nodes in the architecture of the network were used to avoid overfitting [42].

On the one hand, on-line back propagation training algorithms, hyperbolic tangent-type function for the hidden nodes and logistic-type transfer functions for the output layer neurons were chosen to fit the network for ethanol classification. The optimal network topologies (architecture and number of neurons in the hidden layer) were selected by testing several MLFF network structures and functions. Finally, the accuracy of the model was given by the correct classification rate (CCR%) and the confusion matrix.

On the other hand, a single hidden layer and quick propagation training algorithms (a modified version of the back propagation algorithms) showed the best results to predict ethanol concentrations in pineapple waste [43]. Logistic-type transfer functions for both output layer neurons and hidden nodes were selected by testing several artificial neural network structures and functions. Finally, the accuracy of the obtained model was also given by the RMSEP and R^2.

3. Results and discussion

3.1. Multivariate analysis of the obtained EIS response

For each analyzed sample, the AVISPA device generated 200 data corresponding to the modulus and phase of the 100 applied frequencies (between 1 and 10^6 Hz, in linear steps of approximately 10100 Hz). The modulus graph did not reveal important information whereas the representation of the average phase values demonstrated that frequencies between 6.0×10^5 Hz and 8.0×10^5 Hz (21 frequency data) showed the highest sensitivity to ethanol concentration (Figure 1). In fact, the phase of EIS in pineapple waste samples for this frequency range decreased as the added ethanol concentration increased. This decrease is observed in all the selected frequencies. Therefore, we obtain parallel plots, with a clear separation among them except for those corresponding to concentrations 2.5% and 5% (nearly overlapped). As a consequence, phase values between 6.0×10^5 Hz and 8.0×10^5 Hz were selected for further data treatment.

[Please, insert Figure 1]

PCA analysis was conducted in order to check the ability of EIS-based technique to quantify the amount of added ethanol in pineapple waste. As shown in the biplot (Figure 2), a clear discrimination of all the samples according to their corresponding ethanol concentration is obtained and they are allocated in ascending order from right to left in the graph. It is also noteworthy that the 99.65% of the total variability can be explained with only two principal components. The first principal component (PC1) and the second principal component (PC2) explained 99.14% and 0.51% of the total variability, respectively. Consequently, ethanol content can be discriminated with only one principal component in the analyzed frequency range.

[Please, insert Figure 2]

Subsequently, PLS analysis was conducted in order to create predictive models to quantify ethanol concentrations from the selected values of phase from EIS analysis in an easy and reliable way. Thus, Figure 3 shows the correlation between experimental values and those obtained by the PLS prediction model using only one latent variable. In this specific case, the model is created by just one latent variable with R^2 = 0.974 and RMSEP = 1.0588. Therefore, the designed model is considered statistically valid to predict ethanol content in pineapple waste from electrochemical signals.

[Please, insert Figure 3]

3.2.Modeling by Fuzzy ARTMAP neural networks

ANNs usually outperform multivariate methods in electrochemical applications [44] such as for fermentable sugar identification and quantification [20] and saccharification monitoring [21]. Moreover, ANNs can be implemented in programmable components to build portable devices as stated before. Therefore, data classification was performed by using Fuzzy ARTMAP neural networks. In order to reach a compromise between a high rate and a minimum mapfield, the ρ and β values have been changed in the range of [0.1-1.0]. For each combination, the mapfield size and the recognition rate were calculated (Tables 1 and 2, respectively). Therefore, a small sized mapfield has been obtained with ρ values in the range of [0.1-0.6] and β = 0.8 with a maximum recognition rate of 94.4%, getting a mapfield of 10.

Table 1. Mapfield for EIS phase data from 6.0×10^5 Hz to 8.0×10^5 Hz.

	Mapfield						
β / ρ	**0.4**	**0.5**	**0.6**	**0.7**	**0.8**	**0.9**	**1.0**
0.1	17	13	100	12	10	11	10
0.2	17	13	100	12	10	11	10

0.3	17	13	100	12	10	11	10
0.4	17	13	100	12	10	11	10
0.5	17	13	100	12	10	11	10
0.6	17	13	100	12	10	11	10
0.7	17	13	100	12	11	11	10
0.8	18	14	100	13	11	11	12
0.9	100	16	100	100	17	17	16

Table 2. Recognition rates for EIS phase data from 6.0×10^5 Hz to 8.0×10^5 Hz.

	Recognition rate						
β / ρ	**0.4**	**0.5**	**0.6**	**0.7**	**0.8**	**0.9**	**1.0**
0.1	83.33	77.77	88.88	88.88	94.44	88.88	88.88
0.2	83.33	77.77	88.88	88.88	94.44	88.88	88.88
0.3	83.33	77.77	88.88	88.88	94.44	88.88	88.88
0.4	83.33	77.77	88.88	88.88	94.44	88.88	88.88
0.5	83.33	77.77	88.88	88.88	94.44	88.88	88.88
0.6	83.33	77.77	88.88	88.88	94.44	88.88	88.88
0.7	83.33	77.77	88.88	88.88	94.44	88.88	88.88
0.8	83.33	77.77	88.88	88.88	94.44	88.88	88.88
0.9	72.22	61.11	72.22	77.77	77.77	77.77	72.22

As a result, β = 0.8 and ρ = 0.6 values were chosen and the obtained confusion matrix is shown in Table 3. The diagonal cells (in green) indicate the number of residue positions that were correctly classified for each of the 6 ethanol concentrations. The off-diagonal cells (in orange) represent the number of residue positions that were misclassified. The grey cells show the total percentage of correctly predicted residues (top number in green color) and the total percentage of incorrectly predicted residues (bottom number in red color). As seen in Table 3, the designed Fuzzy ARTMAP neural network successfully matched 17 (94.4%) in 18 test measurements and failed in only one of them (5.6%). The prediction failure corresponds to a 2-type measurement (ethanol concentration of 2.5%) that has been classified as a 3-type (ethanol concentration of 5%). These results are consistent with those obtained in the PCA analysis (Figure 2), where samples with 2.5% and 5% of ethanol content were clearly and only separated according to PC2 parameter. Finally, it is important to note that PC1 explained 99.14% of the total variability whereas PC2, 0.51%.

Table 3. Confusion matrix obtained with the Fuzzy Artmap ANN for EIS phase data from 6.0×10^5 Hz to 8.0×10^5 Hz. Target Class: 1: (0% v/v), 2: (2.5% v/v), 3: (5% v/v), 4: (7.5% v/v), 5: (10% v/v), 6: (20% v/v)

		Target Class						
		1	**2**	**3**	**4**	**5**	**6**	
Output Class	**1**	3 16.7%	0 0.0%	0 0.0%	0 0.0%	0 0.0%	0 0.0%	100% 0.0%
	2	0 0.0%	2 11.1%	0 0.0%	0 0.0%	0 0.0%	0 0.0%	100% 0.0%
	3	0 0.0%	1 5.6%	3 16.7%	0 0.0%	0 0.0%	0 0.0%	75.0% 25.0%
	4	0 0.0%	0 0.0%	0 0.0%	3 16.7%	0 0.0%	0 0.0%	100% 0.0%
	5	0 0.0%	0 0.0%	0 0.0%	0 0.0%	3 16.7%	0 0.0%	100% 0.0%
	6	0 0.0%	0 0.0%	0 0.0%	0 0.0%	0 0.0%	3 16.7%	100% 0.0%
		100% 0.0%	66.7% 33.3%	100% 0.0%	100% 0.0%	100% 0.0%	100% 0.0%	94.4% 5.6%

3.3.Modeling by MLFF neural networks

Different MLFF network architectures were tested in order to determine the number of neurons in the hidden-layer and optimize the fitting between the ethanol content and the EIS data set. As a consequence, a 21-6-6 architecture was designed that means 21 input nodes (corresponding to the 21 analyzed frequencies) connected to a 6-node hidden layer and a final 6-output layer (representing the 6 different concentrations of ethanol in to which the data has to be classified). The confusion matrices generated by the MLFF model for the corresponding training, validation and test phases are shown in Table 4. In the confusion matrices, diagonal cells (in green) show the number of data that were correctly classified for each ethanol concentration. The off-diagonal cells (in orange) indicate the number of data that were misclassified. Therefore, these results demonstrate that the designed MLFF is an accurate and reliable model for determining ethanol concentrations depending on EIS measurements (CCR% = 96.15%). Similarly, errors in the range of 2.5% and 5% were observed with that method as a consequence of the overlapped data set for the above mentioned concentrations.

Table 4. Confusion matrices for the added ethanol concentrations (%) for EIS phase data from 6.0×10^5 Hz to 8.0×10^5 Hz (CCR%: correct classification rate).

	Mean CCR% = 96.15%																							
	Training						**Validation**						**Test**						**Overall**					
Target (%) / Output (%)	**0**	**2.5**	**5**	**7.5**	**10**	**20**	**0**	**2.5**	**5**	**7.5**	**10**	**20**	**0**	**2.5**	**5**	**7.5**	**10**	**20**	**0**	**2.5**	**5**	**7.5**	**10**	**20**
0	7						1						1						9					
2.5		6						0	1					1	1					7	2			
5			7						1						1						9			
7.5				6						2						0						8		
10					6						2						1						9	
20						5						1						2						8

Finally, a 21-10-1 architecture was designed to quantify ethanol in pineapple waste samples that means 21 input nodes connected to a 10-node hidden layer and a final output layer. The obtained statistics for the corresponding training, validation and test phase and the scatter plot showing the correlation between predicted and added ethanol concentrations are shown in table 5 and figure 4 respectively. Consequently, accurate and reliable ANN-based models were designed to quantify ethanol in pineapple waste. Particularly, the best fit was obtained by MLFF as it can be seen by comparing R^2 and RMSEP parameters for both PLS and ANN models.

Table 5. Artificial neural network (ANN) results for the studied ethanol concentrations for EIS phase data from 6.0×10^5 Hz to 8.0×10^5 Hz (R^2: coefficient of determination; RMSE: Root Mean Square Error).

	R^2	RMSEP
Training	0.996	0.399
Validation	0.997	0.308
Test	0.996	0.408

[Please, insert Figure 4]

4. Conclusions

The use of the AVISPA device associated to a stainless steel double needle electrode has allowed the application of a specific EIS frequency sweep [0.01 Hz - 10 MHz] for ethanol quantification in real pineapple waste samples. The tests performed with this technique and PCA analyses have shown that is possible to discriminate different concentrations of ethanol using the phase data in frequencies from 6.0×10^5 Hz to 8.0×10^5 Hz. Further PLS analyses have accurately correlated EIS data to ethanol concentrations in the samples (R^2=0.974 and RMSEP = 1.0588). Therefore, it is shown that ethanol concentration in pineapple waste samples can be quantified by EIS.

Moreover, different ANNs (Fuzzy ARTMAP and MLFF) have been studied in order to generate mathematical models able to be implemented into programmable systems. Results show that the appropriate combination of EIS assays and ANN (MLFF) analyses of the data is able to quantify ethanol content in pineapple waste samples in an accurate and reliable way (R^2 = 0.996 and RMSEP = 0.408).

Finally, the obtained results are very promissory in the field of monitoring bioethanol production from lignocellulosic wastes due to a twofold reason: a) the obtained results allow us to suggest the implementation of ANN-based mathematical models on portable, easy and low cost EIS-based measurement systems to quantify ethanol production along the fermentation processes and b) this technique can be successfully applied not just in monitoring the pineapple waste fermentation process but in managing bioethanol production from many other similar lignocellulosic wastes.

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Conflict of Interests

The authors declare no conflict of interests regarding the publication of this paper.

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