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Short communication

Monitoring of solid-state fermentation of protein feed by electronic nose and chemometric analysis

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ABSTRACT

To achieve the real-time smell monitoring of solid-state fermentation (SSF) of protein feed associated with its degree of fermentation. Electronic nose (e-nose) technique, with the help of chemometric analysis, was attempted in this study. Linear discriminant analysis (LDA), *K*-nearest neighbors (KNN), and support vector machines (SVM) were respectively used to calibrate discrimination models in order to evaluate the influences of different linear and non-linear classification algorithms on the identification results. Experimental results showed that the predictive precision of SVM model was superior to those of the others two, and the optimum SVM model was obtained when five *PCs* were included. The discrimination rates of the SVM model were 97.14% and 91.43% in the training and testing sets, respectively. The overall results sufficiently demonstrate excellent promise for the e-nose technique combined with an appropriate chemometric method to be applied in the SSF industry.

1. Introduction

Agricultural residues are the most abundant resource in China with an annual production rate of about 700 million tons which can be microbiologically converted into protein feed products for animals [1]. Most of the agricultural by-products are poor in nutrition such as protein and vitamin and are rich in fiber with low digestibility and are not suitable for non-ruminant animals [2]. Under such circumstances, a potential solution is available by the utilization of microorganisms to convert agricultural wastes into obtain products with higher nutritive value and digestibility, especially in regard to protein content. Bioconversion of these materials by the process of solid-state fermentation (SSF) is often used due to its low effluent generation, requirement for simple fermentation equipment and the direct applicability of the fermented product for feeding [3,4]. SSF is a complex process in which raw materials are transformed into high-value product (e.g. agricultural residue into protein feed). The fermentation process is, however, sensitive to many factors, which can cause the target product to deteriorate. Smells of the products are vital factors in the fermentation industry and subsequently much time and effort are spent on methods that can estimate and measure these factors [5]. In fermentation, only gas chromatography, in some cases combined with mass spectrometry is commonly used [6–9]. Head space gas chromatography combined with mass spectrometry (GC/MS) can identify and quantify the composition of volatile organic compounds (VOCs), giving a complex pattern. The problem is that even if the composition is known, it is still difficult to couple this pattern to the quality of the fermentation. Thus, it appears that a simple but yet powerful objective method for the description of fermentation parameters related to smell would be very valuable.

There is today a great interest in using an electronic nose (e-nose) system for detection and discrimination of volatile compounds. The sensor array in the e-nose system consists of some non-specific sensors, and an odor stimulus generates a characteristic fingerprint from the sensor array [10]. The e-nose technique as an increasingly fast, reliable and robust technology has been successfully applied in different fields such as food [11–14], clinical diagnostics [15–17], pharmaceutical [18], environmental control [19–21]. Recently, the e-nose technique, most noteworthy, has been also employed in recognition and quality analysis of various fermentation [22–27]. These studies mentioned above show that the e-nose technique has high potential in discrimination and quality monitoring of the fermentation process. However, little attention, up to the present, has been reported on the process monitoring of SSF of protein feed by the use of e-nose technique; additionally, the experiments were performed in the commercial e-nose instrument; and they have also not systemically studied different linear and non-linear discrimination algorithms in the solution to the identification of fermenting degrees by the use of the e-nose data.

The e-nose device usually consists of an array of different metal oxide semiconductor (MOS) gas sensors with overlapping sensitivities toward volatile gas components. Normally, the gas sensors

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have non-specific sensitivity toward volatile gas components in SSF of protein feed. Thus, there are significant correlations existing in two different gas sensor data, and this data information is often called the redundant information. The performance of the discrimination model based on e-nose data might be weakened because of involving too much redundant information. However, this problem can be effectively solved with the help of multivariate data calibration technique. In multivariate calibration, a discrimination model based on supervised pattern recognition method (that is, a method with a priori knowledge about the category membership of samples) is used for identification [28]. First, a discrimination model is developed by the use of a training set of samples with known categories; then, the model performance is evaluated by means of the independent samples from a testing set by comparing the prediction with the true categories [29]. Supervised pattern recognition methods are numerous, and the crucial problem is to select the most appropriate method.

In this study, we evaluate the use of an e-nose technique for monitoring of the fermented process of SSF of protein feed by calibrating an identification model. The specific research work was arranged as follows: (1) an e-nose system based on the gas sensor array was developed for data acquisition of fermented samples; (2) latent variables were extracted from the responses of gas sensors and (3) three different linear and non-linear discrimination tools, which were linear discriminant analysis (LDA), *K*-nearest neighbors (KNN) and support vector machine (SVM), were used to develop the discrimination models, respectively.

2. Materials and methods

2.1. Sample preparation

Samples were prepared at different times from four runs of SSF of protein feed trials. The rice chaff was obtained from the Zhenjiang city of Jiangsu Province of China. It was mixed with corn flour and wheat bran (rice chaff:corn flour:wheat bran was 7:2:1), and then the mixtures were ground by use of a crushing machine with 40 mesh screen. Finally, the basal substrates, which were made up of mixture of effective microorganisms (EM) bacterial liquid, water and the pretreated mixtures in the ratio of 1:200:500, were loaded in GTG-100 bioreactor (100 L) with a 40% occupancy coefficient of the bioreactor volume, and cultures were incubated by anaerobic fermentation at 30 ± 2 °C for six days. The samples were obtained from the four runs of fermentation, and in each run, 35 samples were collected. Every day, 5 samples were taken out for signal acquisition of the e-nose system, thus 140 samples date were obtained in this process.

In this study, all 140 fermented samples were divided into two subsets (i.e. training set and testing set). The training set contained 105 samples from the first three runs of fermentation experiments, and the remaining 35 samples from the last run of fermentation trial constituted the testing set.

2.2. Data acquisition and latent variable extraction

The original data were obtained by the use of an electronic nose (e-nose) system, which was designed and developed by the Agricultural Product Processing and Storage Lab of Jiangsu University. Based on the fermentation, a series of trials were carried out using a number of commercially available metals oxide semiconductor (MOS) gas sensors. From the response sensitivity of individual sensor toward the VOCs of fermented materials, a set of eleven gas sensors from Figaro Co. Ltd., Japan (i.e. universal sensors of TGS2602, TGS2610, TGS2611, TGS813, and TGS822, special sensors of TGS822TF, TGS825, TGS826, TGS880, TGS4160, and TGS5042) were eventually selected for odor capture in the SSF process of protein feed. In the e-nose system, the gas sensors are very sensitive to temperature, which strongly influences the electrical properties of MOS. Thus, a temperature sensor was embedded in the sensor chamber. There is an adjustable temperature controller existing in the e-nose system which can control the sampling temperature of the sensor array. During the experiment, the ambient temperature is pre-set at 22 °C in the laboratory. In order to maintain the temperature at around 22 °C in the sensor chamber, the temperature controller begins to work while the temperature in the sensor chamber exceeds the ambient temperature, i.e. 22 °C, and cannot stop until the temperature is going back to 22 °C. In addition, the humidity is kept at a level of 65% in the laboratory.

The e-nose experimental cycle consists of the automated sequence of internal operations for each sample contained the following three stages: (i) headspace generation, (ii) sampling, and (iii) purifying. The experimental conditions of the e-nose system in this study are given as follows: amount of each fermented sample = 6 g, temperature = 22 ± 1 °C, headspace generation time = 120 s, sampling time = 120 s, purging time = 180 s, and airflow rate = 3 mL/s. The maximum value of the response of each sensor was extracted as the latent variables. Thus, eleven latent variables can be obtained from raw e-nose data, which were marked as $p_1, p_2, \ldots, p_{11}$, respectively.

2.3. Software

Software of e-nose data acquisition was compiled by us based on Delphi 7 (Borland, Scotts Valley, USA). All algorithms were implemented in PASW Statistics 18 (IBM, New York, USA) and Matlab R2010a (Mathworks, Natick, USA) under Windows 7 in data processing.

3. Results and discussion

3.1. Principal component analysis (PCA)

In the e-nose system, eleven non-specific metal oxide semiconductor gas sensors have cross-sensitivity toward VOCs in fermented substrate. Thus, there are collinear variables existing in the eleven latent variables, which also can be proved by the use of the results of Pearson correlation analysis (see Table 1). This problem could be solved with the help of principal component analysis (PCA). PCA is a method of describing the unique variances in a set of original variables using linear combinations of the original variables (principal components, *PCs*), and these *PCs* are orthogonal [30]. In this study, PCA was performed on eleven latent variables, and several of the *PCs* were extracted as the input of supervised pattern recognition. To visualize the cluster trends of all 140 samples, a scatter plot (also called a score plot) was obtained using the top two *PCs* issued from PCA based on eleven latent variables.

Fig. 1 shows a two-dimensional (2D) space of all fermented samples represented by *PC1* and *PC2*. Investigated from Fig. 1, seven sample groups appeared in cluster trend along two principal component axes, confirming the presence of seven different clusters

Table 1
Pearson correlations among eleven latent variables.

Variables	Pearson correlations										
	p_1	p_2	p_3	p_4	p_5	p_6	p_7	p_8	p_9	p_{10}	p_{11}
p_1	1	−0.742[a]	0.727[a]	−0.357[a]	0.791[a]	0.729[a]	−0.275[a]	0.483[a]	0.234[a]	0.640[a]	−0.240[a]
p_2		1	−0.234[a]	0.554[a]	−0.303[a]	−0.205[b]	0.732[a]	0.053	−0.243[a]	−0.653[a]	0.705[a]
p_3			1	−0.280	0.942[a]	0.963[a]	0.377[a]	0.897[a]	0.136	0.530[a]	0.388[a]
p_4				1	0.122	0.118	0.738[a]	0.391[a]	−0.070	−0.675[a]	0.730[a]
p_5					1	0.984[a]	0.347[a]	0.900[a]	0.154	0.383[a]	0.383[a]
p_6						1	0.430[a]	0.927[a]	0.138	0.374[a]	0.461[a]
p_7							1	0.688[a]	−0.117	−0.372[a]	0.979[a]
p_8								1	0.083	0.211[b]	0.686[a]
p_9									1	0.230[a]	−0.145
p_{10}										1	−0.433[a]
p_{11}											1

[a] Correlation is significant at the 0.01 level (2-tailed).
[b] Correlation is significant at the 0.05 level (2-tailed).