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Monitoring of fermentation process parameters of Chinese rice wine using attenuated total reflectance mid-infrared spectroscopy

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ABSTRACT

There is a growing need for the effective fermentation monitoring during the manufacture of wine due to the rapid pace of change in the industry. In this study, the potential of attenuated total reflectance mid-infrared (ATR-MIR) spectroscopy to monitor time-related changes during Chinese rice wine (CRW) fermentation was investigated. Interval partial least-squares (i-PLS) and support vector machine (SVM) were used to improve the performances of partial least-squares (PLS) models. In total, four different calibration models, namely PLS, i-PLS, SVM and interval support vector machine (i-SVM), were established. It was observed that the performances of models based on the efficient spectra intervals selected by i-PLS were much better than those based on the full spectrum. In addition, nonlinear models outperformed linear models in predicting fermentation parameters. After systemically comparison and discussion, it was found that i-SVM model gave the best result with excellent prediction accuracy. The correlation coefficients (R^2 (pre)), root mean square error (RMSEP (%)) and the residual predictive deviation (RPD) for the prediction set were 0.96, 6.92 and 14.34 for total sugar, 0.97, 3.32 and 12.64 for ethanol, 0.93, 3.24 and 9.3 for total acid and 0.95, 6.33 and 8.46 for amino nitrogen, respectively. The results demonstrated that ATR-MIR combined with efficient variable selection algorithm and nonlinear regression tool as a rapid method to monitor and control CRW fermentation process was feasible.

1. Introduction

Chinese rice wine (CRW), a traditional alcoholic beverage in China, has a history of more than 5000 years. It is one of the most popular alcoholic beverages with an annual consumption of more than 2 million kiloliters in China, especially in the south (Li, Wang, Huang, Pan, & Li, 2013; Shen et al., 2012). CRW fermentation was initially hand-crafted and controlled through organoleptic evaluations conducted by experienced winemaking experts who were able to estimate the situation of the fermentation process. In the past few decades, due to the realization of CRW industrialization; the empirical evaluation of the fermentation process is replaced by the control of several critical parameters such as pH and total acid. Although the traditional methods have a high accuracy, they usually require expensive devices and complicated sample preparation or purification, which delays the acquisition of real-time information. Consequently, stuck or sluggish fermentation occur in CRW winery and cause severe damages frequently. Therefore, there has been a growing need in developing methods which are not only accurate, but also rapid and inexpensive for detecting real-time information of the fermentation process in the latest few years.

As a rapid and non-destructive technique, infrared spectroscopy (IR) technique, has been gradually developed as an alternative to wet chemistry in the food industry during the last few years (Cozzolino & Curtin, 2012; Shen et al., 2010). Due to the rapidity and easiness, a large number of studies have been conducted with the application of Fourier-transformed near infrared spectroscopy (FT-NIR) in wine industry (Grassi, Amigo, Lyndgaard, Foschino, & Casiraghi, 2014; Juan, López, lSánchez, García, & Morales, 2008). However, compared with FT-NIR, there is less study on the application of Fourier-transformed mid-infrared spectroscopy (MIR) in wine industry. Compared with FT-NIR, whose peaks are broad and overlapping, MIR spectroscopy generally exhibited sharper absorption bands and yield more distinct spectral features. Therefore it may provide a more precise determination of various components or properties than FT-NIR technique (Cozzolino & Curtin,

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2012; Cozzolino, Cynkar, Shah, & Smith, 2011). In recent years, there has been increasing attention on the application of MIR technology in the food industry (Bauer et al., 2008; Regmi, Palma, & Barroso, 2012; Urtubia, Pérez-correa, Pizarro, & Agosin, 2008). MIR spectrophotometers used for wine routine analysis are usually equipped with a transmission cell that was able to provide precise measurements. However, the use of transmission cells also brings some obvious disadvantages, such as filling and cleaning of the cell and variation of the sample path length. The development of attenuated total reflectance (ATR) sampling technique has brought significant improvements in the routine analysis, by eliminating the procedure of sample preparation and overcoming measurement problems usually caused by using transmission cells (Cozzolino et al., 2011; He, Duan, & Ma, 2013).

Due to the strong peak overlapping of IR spectra, the application of powerful mathematical techniques is essential for wine analysis (Schenk, Marison, & von Stockar, 2007). Partial least squares (PLS), a classical multivariate regression method, has been widely used for developing models in wine industry using data from IR spectra (Fragoso, Acena, Guasch, Mestres, & Busto, 2011; Urtubia, Perez-Correa, Meurens, & Agosin, 2004). However, the prediction accuracy of the full spectrum PLS model is susceptible to water absorption and other unrelated or collinear spectral variables for wine samples (Ouyang, Chen, Zhao, & Lin, 2012). Therefore, spectra variables selection is needed to improve the performance of the full-spectrum calibration techniques. With the help of interval partial least-squares (i-PLS), we can focused on the important spectral regions and remove interferences from other regions (Norgaard et al., 2000). In addition, in consideration of the complexity of the correlation between the IR spectra and wine constituents, linear regression models may not give a perfect solution to the modeling problem. In these cases, methods for linear modeling of nonlinear surfaces are needed. Support vector machine (SVM), proposed by Vapnik, is a promising method to fulfill this goal (Shi et al., 2013). Due to its attractive advantages and excellent performances comparing with other conventional learning algorithms such as back propagation artificial neural network (BP-ANN) and linear discriminant analysis (LDA), SVM has been widely applied in many fields (Bao et al., 2014; Q. Chen, Ding, Cai, & Zhao, 2012).

In the CRW industry, IR spectroscopy combined with chemometrics has been used to simultaneously determine various components in the final product (Yu, Ying, & Lu, 2006). Nevertheless, until now, there were few studies focused on the use of IR spectroscopy for CRW fermentation control. The fermentation monitoring technique of CRW industry has fallen far behind the other wine industries in the developed country. Furthermore, previous studies regarding fermentation monitoring mainly focused on linear regression (PLS) models, litter research exists on nonlinear regression models (Grassi et al., 2014). Therefore, the purpose of this study was to investigate the possibility of ATR-MIR spectroscopy combined with spectra variables selection algorithm and nonlinear tool for monitoring and assessment of changes during the CRW fermentation process.

2. Materials and methods

2.1. Fermentation trials and sampling

In order to develop robust and stable multivariate models, four most frequently used manufacture processes in CRW industry, namely, enzymatic extrusion pretreatment technique (EEP), liquefaction pretreatment technique (LP), two-step fermentation (TSF) and simultaneous saccharification and fermentation (SSF), were used in this study. The four different manufacture processes were conducted as follows:

2.1.1. EEP fermentation

The rice extrudate (4000 g, db) was collected in 16 L fermentor with 8 L water, 4 g yeast (*Saccharomyces cerevisiae*, China General Microbiological Culture Collection Centre) and 640-g wheat Qu (Zhejiang Nv'erhong Shaoxing Wine Co. Ltd.). After agitation, the broth was incubated at 30 °C for 5 days (main fermentation) and then incubated at 15 °C for 15 days (post-fermentation).

2.1.2. LP fermentation

The crushed rice powder (4000 g, db) was mixed with 8 L water and 0.35 g thermostable α-amylase (Termamyl 120 L, Novozymes, Denmark), then the mixture was incubated at 100 °C for 10 min and cooled to room temperature. Then 4 g yeast and 640 g wheat Qu were added into the fermentor, after that it was fermented in the same way as described in EEP fermentation.

2.1.3. TSF fermentation

The steam-cooked rice (4000 g, db) was mixed with wheat Qu (640 g) and placed in the fermentor for 24 h, leaving a hole in the middle of the fermentation in order to promote the saccharification of cooked rice, after that 8 L water and 4 g yeast were added into the fermentor and fermented in the same way as described above.

2.1.4. SSF fermentation

The steam-cooked rice (4000 g, db) was collected in the same fermentor and 8 L water, 4 g yeast and 640 g wheat Qu were added into the fermentor. After that, it was fermented as aforementioned.

We proceeded with three trials for each kind of manufacture process. In total, twelve micro-fermentation trials were performed in this study. For each micro-fermentation trial, samples were collected at thirteen times during CRW fermentation (0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 15 and 20 days) after the fermentation process started, with a total of 156 samples. All samples were centrifuged for 15 min at 5000 g to separate a clear solution from fermentation broth. The clear supernatant was mixed with sodium azide to fix the sample (limit the growth of bacteria) and stored at 4 °C until further analysis.

2.2. Reference analysis

Total sugar (g/L), total acid (g/L), ethanol (g/L) and amino acid nitrogen (g/L) were the oenological parameters used to monitor the CRW fermentation. These parameters were determined as follows.

2.2.1. HPLC determination of ethanol content

Ethanol content was determined by the method of Egidio et al. (Di Egidio, Sinelli, Giovanelli, Moles, & Casiraghi, 2010). It was carried out using HPLC (ShimadzuRID-10A system, Japan) equipped with an exclusion column (BIORAD-Aminex Ion Exclusion HPX-87H, 300 mm $\times$ 7.8 mm) at 60 °C with a mobile phase of sulfuric acid (2.5 mM) at a flow rate of 0.5 ml/min. The analysis was carried out in duplicate.

2.2.2. Determination of total reducing sugar (TS), total acid (TA) and amino acid nitrogen (AAN)

The total reducing sugar content of the supernatant wine was determined by the 3,5-dinitrosalicylic acid colorimetry (DNS) method (Jin, Xu, & Li, 2013). Reference analyses for TA and ANN were in accordance with the official methods of analysis for Chinese rice wine (GB/T 13662-2008). Briefly, wine samples (10 mL) were mixed with 50 mL distilled water and titrated to end point of pH = 8.2 with 0.1 M NaOH; the volume of consumed NaOH was