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Precision Test for Monitoring of Acetification Process in Vinegar Fermented Bioreactor using Near-Infrared Spectroscopy

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Abstract

Near infrared (NIR) spectroscopy is known as a fast and reliable technique to analyse physical and chemical properties of different analyte. The main objective of this paper is to test for the precision of NIR spectrometer by evaluating scanning repeatability and reproducibility for measuring acetic acid (AA) and ethanol (ET) on acetification rate (ETA) of rice vinegar and its corresponding reference method using acid-base titration with NaOH and gas chromatography, respectively. Results show that the repeatability and reproducibility of NIR scanning spectrometer is 0.0206 and 0.1346. The repeatability of reference method for AA and ET were 0.01 and 0.04, respectively. The maximum co-efficient of determination (R^2_{MAX}) were 0.996 and 0.998, respectively.

Keywords: Acetic acid, Ethanol, Acetification rate, Vinegar, Precision.

1. Introduction

Vinegar is a popular seasoning that adds taste in the food. Vinegar is fermented from rice, corn, fruit or sugar. (Pornchaloempong and Rattanapanon, 2014) Fermented sugar becomes alcohol by yeast and fermented alcohol become acetic acid by aerobic bacteria to get acid of sour taste known as Vinegar.

Rice vinegar (Foster, 2016) made by fermenting the sugars in rice first into alcohol, and then into acid. Compared to white distilled vinegar, rice vinegar is less acitic with a delicate, mild, and somewhat sweet flavor. Rice vinegar is ranged in different color, from clear to different shades of white and red; each variety has a slightly different taste. White rice vinegar (Wan, 2016) is slightly yellow in color, with higher acetic acid than other Chinese vinegar, is less acitic and milder in flavor than Western vinegar. Brown rice vinegar (Han, 2013) is slightly light to dark brown in color.It is made from unpolished brown rice, this version of rice vinegar are supposed to have higher nutrients. Black rice vinegar is deeper in color and flavor, it has somewhat smoky-taste. Vinegar is made from black glutinous rice and other grains like wheat, millet, and sorghum. It is often used in Chinese stir fries, dipping sauces, and as a condiment. Red rice vinegar is made from red yeast rice (fermented rice) and sometimes barley and sorghum, it is sweet and salty. Seasoned rice vinegar is white rice vinegar with added sugar and salt.

Acetic acid (Garcia, 2016), also known as ethanoic acid and methane carboxylic acid, is a colorless liquid that has a strong and distinct pungent and sour smell. It is an organic compound. Each year, a million tons of acetic acid is produced. Acetic acid is used in vinegar in large amount. It is very important chemical that is used in many industrial processes.

Ethanol (Garcia, 2016) is a chemical compound that is present in many things that we use on a daily basis, from perfumes to alcoholic beverages. Ethanol is a simple chemical compound, but it has so several uses. It is used as antiseptics, household cleaning products and even in varnishes.

In the process of fermenting rice vinegar by Actic Acid Bacteria (AAB) in tank, we measure the impact of concentration of acetic acid (AA) and of Ethanol (ET) on acetification rate (ETA) everyday. AA is determine by acid-base titration with NaOH using phenolphthalein as indicator and ET is analyze by Ebullionmeter.

Near Infrared (NIR) Spectroscopy is a rapid technique for non destructive testing. The NIR spectroscopy emit radiation on the sample and molecules of sample absorb energy from radiation that cause vibration in overtone and

combination mode. The spectra obtained from NIR scanning pre-treated with mathematic methods to erase the unwanted disturbance. The relationship with constituent data by chemical methods or other reference method is developed using Chemometrics.

Robust NIR model can be developed when there is minimal error during the process of scanning and reference method. So, the precision of the instrument is measured by the value of repeatability and reproducibility. Maximum coefficient of determination (R^2_{max}) can indicate whether the model should be further developed or not. We, therefore need to determine repeatability, reproducibility and R^2_{max} of NIR scanning instrument and method used to obtain reference value.

2. Materials and Methods

2.1 Materials.

Rice vinegar was prepared from sticky rice in the Laboratory of Fermentation Technology, Faculty of Agro-Industry.King Mongkut's Institute of Technology Ladkra-bang, Bangkok, Thailand, and used as the raw materials for acetification in the internal Venturi injector bioreactor (Krusong, Yaiyen and Pornpukdeewatana, 2014). The ET andAA in rice wine were 110 ± 1.5 g l-1 and 2.5 ± 0.4 g l-1, respectively, while AA content in the vinegar was 80 ± 0.8 g l-1. This was standardized by adjusting the ET and AA contents to give a target total solute concentration (TC) such as 35 ± 1 g l-1 ET and 45 ± 1 g l-1 AA for a TC of 80 g l-1.

2.2 NIR scanning of rice vinegar.

FT (Fourier transform)-NIR spectrometer (Bruker Ltd., Germany) was used for scanning. Each sample was transferred into a glass vial of 22.0 mm diameter and 48.0 mm height, as a measurement cell. Covered with a transflection plate made from aluminum which provided an optical path length of 0.1 mm and scanned between wavenumber of 12,500 - 4000 cm^{-1} (800 - 2500 nm) with a resolution of 16 cm^{-1}. The scanning was completed 32 times per one average spectrum. Before each sample scanning, the gold used as a reference material was scanned for background. All scanning was conducted at air conditioning room temperature (25.0 ± 2.0℃) but sample at 0.0°±1.0℃.

2.3 Analytical method.

The acidity (%v/v) of the finished product after acetification was determined by acid-base titration with 0.1 mol^{-1} NaOH using phenolphthalein as an indicator. ET was analysed by Ebullionmeter.

2.4 Repeatability, Reproducibility and Maximum coefficient of determination.

Repeatability of NIR scanning was determined by scanning the same sample 10 times in the same position, then finding standard deviation (SD) value of the absorbance of the scanning. We selected 3 wavelength from overall spectrum and SD of absorbance in each wavelength give the repeatability of scanning instrument We selected wavenumber at 10309.0 cm-1 (970 nm), 6896.6 cm-1 (1450 nm) and 5154.6 cm-1 (1940 nm) which were the vibration bands of water. Water is important element in vinegar.

Reproducibility of NIR scanning was determined by scanning the same sample 10 times but re-load sample every time. SD of absorbtion in selected wavelength give reproducibility of the scanning. We selected same wavelengths as for repeatability.

Repeatability of reference method (Rep) is for standard measurement. This can be determined by SD value of the maximum difference in repetition of the same sample for all samples.

Maximum coefficient of determination (R^2_{max}) is the highest possible R^2 for the experiment. This is possible when there is no error in NIR spectrometer. There is only error from the reference test. And R^2_{max} calculated by the following formula

$$R^2_{Max} = \frac{SD_y^2 - Rep^2}{SD_y^2}$$

(1)

where SD_y is the standard deviation of the calibration set data.

3. Results and Discussion

The repeatability and reproducibility of NIR scanning spectrometer is 0.0206 and 0.1346. The repeatability of reference method for AA and ET were 0.01 and 0.04, respectively. The maximum co-efficient of determination (R^2_{MAX}) were 0.996 and 0.998, respectively. The values of Table 1 can be used to determine the precision of the

instrument and reference methods. Because repeatability and reproducibility of NIR scanning was low value, that means there is precision in scanning. And the repeatability of reference method was low and R^2_{MAX} was very high, that means that there is precision in reference methods and it is worth for further developing the model.

Table 1 Repeatability and reproducibility of scanning and repeatability of reference method and maximum coefficient of determination (R2MAX) for acetic acid (AA) and of Ethanol (ET).

Scanning		Parameters	Reference	
Repeatability	Reproducibility		Repeatability	R^2_{max}
0.0206	0.1346	AA	0.01	0.996
		ET	0.04	0.998

4. Conclusions

This research found that with the NIR spectrometer and the reference method have high precision. And it is worth to develop the model for monitoring acetification process in vinegar fermented bioreactor using near-infrared spectroscopy. Therefore, NIR spectroscopy can be used instead of the traditional method if the model is further developed using more samples.

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