Evaluation of a near-infrared spectrophotometer for determining molasses quality

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Abstract This cost-effective, rapid, non-destructive method for measurement of samples without the use of any hazardous reagents was provided to analyze raw sugar and final molasses to assist in improving sugar-mill efficiency and quality control of final products. In addition, it can be used to determine optimal fermentable sugar content to improve ethanol yield during biofuel production. Standard chemical methods were used to analyse 150 final molasses samples and the DS2500 FOSS NIR technique at wavelengths of 400 to 2500 nm was used to develop NIR calibration models. The final molasses calibration model of sucrose showed root mean square (RSQ) and standard error of cross validation (SECV) values of 0.99, 0.17 and 0.32, respectively. Glucose showed 0.99, 0.12 and 0.20, fructose showed 0.98, 0.12 and 0.22, and Brix values showed 0.96, 0.52 and 1.20, respectively. Calibration models showed correlation coefficients of almost 1.0 and biases lower than 0.6 of SEC. The results indicate that NIR is a feasible method for evaluating quality parameters of final products in addition to determining optimal fermentable sugar content.

Key words NIR spectroscopy, sugar production process, molasses, fermentable sugar

INTRODUCTION

The near-infrared spectroscopy (NIR) technique has been adopted widely for sugarcane quality measurements (Madsen et al. 2003; Nawi et al. 2012; Ochola et al. 2015). Polysaccharides, starch, dextran, gum and pectin contents were quantitatively measured in molasses using NIR spectroscopy (Kaur and Kaler 2008). Final molasses is one of the byproducts from the sugarcane value chain and contains fermentable sugars, many minerals and other useful substances.

The principle of NIR spectroscopy is that the sample is exposed to the near-infrared region of the electromagnetic spectrum and has wide application in the food industry. Within molecules, functional groups such as C-H, N-H, O-H, S-H and C=O absorb the radiation (Shenk et al. 1992; Osborne et al. 1993). The aim of our experiment was to apply NIR spectroscopy to analyze the components of final molasses. This cost-effective, rapid, non-destructive method for measurement of samples without the use of any hazardous reagents was developed for determining final molasses quality to improve sugar-mill efficiency and for quality control of final products, as well as determining optimal fermentable sugar content in molasses.

MATERIALS AND METHODS

Material

We obtained 150 samples of final molasses from the central laboratory of Mitr Phol Group. The experiments were conducted at Mitr Phol Innovation and Research Center Co Ltd, Phukieo, Chaiyaphum, Thailand.

Chemical methods

The fermentable content, and sucrose, glucose and fructose levels were measured in final molasses by high-performance liquid chromatography (HPLC) (Shimadzu, Japan) using a Sugar Pak column (Waters Corporation, MS) (ICUMSA Methods GS 7/8/4-24). The sample was diluted to an appropriate concentration, filtered through a 0.45 µm filter and injected into the column using deionized distilled water containing 0.05 g/L disodium calcium EDTA as a mobile phase at 0.5 mL/min.
flow at 80°C. The amount of sugar was quantified using the sugar standard mixtures containing 0.5% sorbitol as an internal standard.

NIR methods

We used a DS2500 FOSS NIR at wavelengths of 400 to 2500 nm for final molasses and developed NIR calibration models. Representative molasses samples for developing NIR calibration models were selected to cover the range of chemical values. Spectra were collected on all samples in the transreflectance mode. The samples were scanned by NIR at wavelengths of 400 to 2500 nm. A folded-transmission gold reflector cup was used with a path length of 0.2 mm.

The equation model was based on input of the chemical value in spectra using the WINISI4 program for development of Partial Least Square Regression (PLS), and we selected the equation from the standard error of cross calibration (SEC), standard error of cross validation (SECV) and standard error of prediction (SEP) values. The samples were separated into two groups, calibration set and validation set. The validation sets were 10% of calibration set.

RESULTS AND DISCUSSION

Results for the analyses of final molasses samples by HPLC for sucrose, glucose, fructose and brix are given in Table 1 and the NIR spectra for molasses are shown in Figure 1.

Table 1. Analyses of the final molasses samples.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Minimum</th>
<th>Maximum</th>
<th>Mean</th>
<th>Standard deviation</th>
<th>Number of samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sucrose (%)</td>
<td>27.51</td>
<td>35.09</td>
<td>30.99</td>
<td>1.83</td>
<td>150</td>
</tr>
<tr>
<td>Glucose (%)</td>
<td>2.80</td>
<td>8.09</td>
<td>5.29</td>
<td>1.17</td>
<td>150</td>
</tr>
<tr>
<td>Fructose (%)</td>
<td>7.14</td>
<td>10.43</td>
<td>8.80</td>
<td>0.81</td>
<td>150</td>
</tr>
<tr>
<td>Brix</td>
<td>68.88</td>
<td>84.98</td>
<td>76.40</td>
<td>3.91</td>
<td>45</td>
</tr>
</tbody>
</table>

Fig. 1. NIR spectra of molasses at wavelengths of 400 to 2500 nm.

A plot of the transreflectance spectra for molasses between 400 and 2500 nm is shown in Figure 1. O’Shea et al. (2011) also reported scanning molasses samples in the transreflectance mode with a NIR instrument, FOSS IX. The absorbance of sucrose, dry substance, pol, brix, reducing sugar and ash were recorded over a wavelength of 578 to 1848 nm.
Calibration model

The calibration mode developed by PLS regression found that sucrose, glucose, fructose and brix of final molasses are at wavelengths of 400 to 2500 nm. RSQs, SECVs, SECs and standard deviations (SD) are shown in Table 2.

**Table 2.** Regression models by PLS of final molasses at wavelengths of 400-2500 nm.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Estimated minimum</th>
<th>Estimated maximum</th>
<th>SD</th>
<th>SEC</th>
<th>RSQ</th>
<th>SECV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sucrose (%)</td>
<td>26.30</td>
<td>35.65</td>
<td>1.56</td>
<td>0.17</td>
<td>0.99</td>
<td>0.32</td>
</tr>
<tr>
<td>Glucose (%)</td>
<td>2.08</td>
<td>8.44</td>
<td>1.06</td>
<td>0.12</td>
<td>0.99</td>
<td>0.21</td>
</tr>
<tr>
<td>Fructose (%)</td>
<td>6.31</td>
<td>11.27</td>
<td>0.83</td>
<td>0.12</td>
<td>0.98</td>
<td>0.22</td>
</tr>
<tr>
<td>Brix</td>
<td>69.52</td>
<td>83.26</td>
<td>2.29</td>
<td>0.52</td>
<td>0.95</td>
<td>1.20</td>
</tr>
</tbody>
</table>

Calibration curve

Calibration curves for sucrose, glucose, fructose and Brix are shown in Figures 2, 3, 4 and 5, respectively.

![Fig. 2. Calibration curve for sucrose.](image1)

![Fig. 3. Calibration curve for glucose.](image2)
External validation

The precision of the calibration model or the external validation compared the wet chemical concentration from the reference method and the predicted value. The statistical analyses of prediction for sucrose, glucose, fructose and Brix content in final molasses are shown in Table 3 - RSQs is more than 0.98, SEPs of Brix and sucrose at 0.06 are lower than for glucose and fructose, and RPD is at a very good level.

Table 3. Statistical analysis of prediction by partial least square regression.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>N</th>
<th>Slope</th>
<th>RSQ</th>
<th>Bias</th>
<th>SEP</th>
<th>SD</th>
<th>RPD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sucrose (%)</td>
<td>15</td>
<td>1.02</td>
<td>1.00</td>
<td>0.00</td>
<td>0.08</td>
<td>1.53</td>
<td>18.94</td>
</tr>
<tr>
<td>Glucose (%)</td>
<td>16</td>
<td>1.02</td>
<td>0.98</td>
<td>0.00</td>
<td>0.14</td>
<td>1.06</td>
<td>7.86</td>
</tr>
<tr>
<td>Fructose (%)</td>
<td>16</td>
<td>1.01</td>
<td>1.00</td>
<td>-0.02</td>
<td>0.06</td>
<td>0.87</td>
<td>15.00</td>
</tr>
<tr>
<td>Brix (%)</td>
<td>5</td>
<td>1.00</td>
<td>1.00</td>
<td>-0.05</td>
<td>0.06</td>
<td>2.91</td>
<td>52.93</td>
</tr>
</tbody>
</table>
CONCLUSION

Our experiment demonstrates the potential of the NIR technique to be a simple, rapid and non-destructive method that can accurately predict the concentration of sucrose, glucose and fructose in final molasses. The result shows the potential of NIR spectroscopy in rapidly determining the concentration of components in final molasses directly without any treatment or dilution. However, increasing the number of samples will improve the prediction ability of NIR.

REFERENCES


Évaluation d’un spectrophotomètre proche-infrarouge pour déterminer la qualité de la mélasse

Résumé. Cette méthode rentable, rapide et non destructive pour la mesure des échantillons, sans l’utilisation de produit chimiques dangereux, peut être utilisée pour analyser le sucre brut et la mélasse finale, afin d’aider à améliorer l’efficacité de la sucrerie et le contrôle de la qualité des produits finis. En outre, elle peut être utilisée pour déterminer la teneur en sucres fermentables optimale pour améliorer le rendement de l’éthanol au cours de la production de biocarburants. Des méthodes chimiques standards ont été utilisées pour analyser 150 échantillons de mélasse finale et la technique DS2500 FOSS NIR aux longueurs d’unne de 400 à 2500 nm; cela a servi à élaborer des modèles d’étalonnage NIR. Le modèle de calibration pour le saccharose de mélasse finale a montré des moyennes (RSQ), des erreurs standards d’étalonnage (SEC) et des écarts-types de validation (SECV) de 0,99, 0,17 et 0,32, respectivement. Le glucose a montré les valeurs de 0,99, 0,12 et 0,20, et le fructose 0,98, 0,12 et 0,22; le Brix montre 0,96, 0,52 et 1,20, respectivement. Les calibrations donnent des coefficients de corrélation approchant 1,0 et des biais inférieurs à 0,6 du SEC. Les résultats indiquent que le NIR est une méthode possible pour évaluer les paramètres de la qualité des produits finis, en plus de déterminer la teneur en sucres fermentables optimale.

Mots-clés: Spectroscopie NIR, processus de production de sucre, mélasse, sucres fermentables

Evaluación de un espectrofotómetro de infrarrojo cercano para determinar calidad de melazas

Resumen. Este método para medición de muestras que tiene costo – beneficio, es rápido, no destructivo, no usa ningún reactivo peligroso, fue previsto para analizar azúcar crudo y melaza final con el objeto de mejorar la eficiencia de la molienda y el control de calidad de productos finales. En adición, puede usarse para determinar el contenido óptimo de azúcar fermentable y mejorar el rendimiento de etanol durante la producción de biocombustible. Se usaron métodos químicos estándares para analizar 150 muestras de melaza final y un equipo DS2500 FOSS NIR de longitudes de onda 400-2500 nm se empleó para desarrollar los modelos de calibración NIR. En el modelo de calibración de sacarosa en melaza final se obtuvieron coeficiente de correlación cuadrático ($R^2$), error estándar de calibración cruzada (SEC) y error estándar de validación cruzada (SECV) valores de 0,98; 0,12 y 0,22, respectivamente. Los valores para glucosa fueron 0,99; 0,12 y 0,20; para fructosa se obtuvieron 0,98; 0,12 y 0,22 los valores de Brix resultaron 0,96; 0,52 y 1,20, respectivamente. Los modelos de calibración presentaron coeficientes de correlación cercanos a 1,0 y diferencias menores a 0,6 de SEC. Los resultados indican que NIR es un método factible para evaluar parámetros de calidad de productos finales además de determinar el contenido óptimo de azúcara fermentables.

Palabras clave: Espectroscopía NIR, proceso de producción de azúcar, melaza, azúcar fermentable