The International Symposium on Agricultural and Biosystem Engineering

BOOK OF ABSTRACTS

"Improving The Role of Agricultural and Biosystem Engineering Toward Food & Energy Self-sufficiency and Sustainable Agriculture"
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Non Destructive Prediction of Ripe-Stage Quality of Mango Fruit Cv ‘Gedong Gincu’ Stored in Low Temperature by NIR Spectroscopy

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Abstract

This study demonstrates the use NIR spectroscopy to predict the internal quality parameter in mango fruit non destructively. Soluble solids content (SSC), pH and firmness of mango fruits cv. ‘Gedong Gincu’) were examined by NIR reflectance to find out factors to be considered in online detection. The wavelength range of 1000–2400 nm was selected and data pre-processing was used to enhance the precision of calibration models based on partial least square (PLS). The coefficient of correlation (r) of SSC, pH and firmness were 0.756, 0.94 and 0.89, and the standard error of prediction (SEP) were 2.10°Brix, 0.157 and 0.63 kgf, respectively. It is concluded that by using the NIR measurement system, in the appropriate spectral range, it is possible to nondestructively predict the ripe-stage quality of mango fruit i.e. SSC, pH and firmness.

Keywords: mango fruit, NIR spectroscopy, internal quality, nondestructive prediction, ripe-stage quality

Introduction

Gedong Gincu is one of the exotic cultivar mango fruit (Mangifera indica L.) in Indonesia due to its sweet taste, medium size and beauty orange color. Mango fruit are usually harvested at the hard green stage (unripe) when they are physiologically mature but before the onset of the climacteric rise (Lakshminarayana et al., 1970). Mature hard green mango fruit attain a superior eating quality when ripe while immature ones do not (Medlicott et al., 1988). After harvesting, the hard green mango fruits are usually directly transported to market. In order to delay the ripening process during long-distance transportation, hard green mango fruits are stored at low temperature condition. Monitoring of quality parameter during this handling step will be very important.

Prediction of ripe-stage quality are usually done by monitoring an external and measuring an internal qualities. Various scientists have considered maturity qualities from different perspectives (Peacock, et al., 1986). Soluble solid content (SSC), pH (acidity) and firmness are the internal quality indices for mango fruits. The methods to measure these internal qualities are still destructive. Therefore, it is essential to develop efficient and non-destructive methods for measuring these internal attributes of mango fruit. Near infrared (NIR) spectroscopy is a fast, easy-to-use and non-destructive analytical technique (Day and Fearn, 1982). NIR spectroscopy has decisive advantages compared to traditional methods.
whereby it analyse sample rapidly (a few seconds per sample) and no need sample preparation (Pissard et al., 2012; Saleh et al., 2012). In addition, it is a chemical-free (limited to the reagents required for reference analyses and no waste is produced (Pissard et al., 2012; Yan et al., 2009), and can be carried out on-line (Saleh et al., 2012).

The use of NIR spectroscopy to measure internal quality attributes of fruits produce has been investigated extensively during the last decade. Use of NIR spectroscopy in fruit is receiving extensive research effort, and commercial applications are in the early stage of implementation (Abbott et al., 1997; Armstrong, 2000). The ability to rapidly 'scan' fruit online, and then sort it, means that if a given characteristic can be accurately measured, fruit can be segregated into distinct classes and either handled or marketed in a different manner.

The variety of studied fruit is large, ranging from apple (Clark et al., 2003; McGlone et al., 2005; Alamar et al., 2007), kiwi fruit (Moghimi et al., 2010), citrus (Kim et al., 2004), mango (Saranwong et al., 2003), mandarin (Guthrie et al., 2005; Gomez et al., 2006), peach (Carlomagno et al., 2004) and pear (Han et al., 2006). More applications and recent developments have been reviewed (Nicolai, 2007). Previous studies have shown that NIR has the capability to evaluate soluble solids content (SSC) in ripe mango fruit (cv. 'Caraboa') (Saranwong et al., 2001, 2003). The objective of this study was to develop calibration model and prediction of the internal quality parameter i.e. Soluble solid content, pH and firmness in mango fruit cv. Gedong Gincu during low temperature condition using NIR spectroscopy.

Materials and methods

Sample Preparation

The 153 mango fruits cv. Gedong Gincu used in this study were randomly divided into two groups of samples: the first group was used to develop the calibration models (103 samples) and the other for predicting quality and model validation purposes (50 samples). All samples had been harvested from the same farmer orchard during one day at commercial maturity or at the level maturity of 80-85 percent. Samples of mango fruits were stored at temperature of 13°C. This was a simulation condition for long distance transportation for mango fruits. Measurement was carried out every 2 days during period storage of 22 days. After acquisition of spectra, SSC was measured using digital Refractrometer, pH was measured using digital pH meter (D-24, HORIBA) and firmness was measured using Rheometer model CR-300.

NIR Spectra Collecting

Spectra of mango fruits were collected in the range of 1000-2400 nm with an increment of 5 nm using NIRflex N-500 (Büchi Labortechnik AG, Flawil, Switzerland) at room temperature of 25°C. Spectra data were collected by measuring the diffuse reflectance of samples. Operation of the instrument and data collection of NIR spectra were conducted by using NIRWare 1.2 software (Büchi Labortechnik AG, Flawil, Switzerland). Chemometric analysis was conducted by using NIRCAL 5.2 software (Büchi Labortechnik AG, Flawil, Switzerland).

A large amount of spectral data is usually obtained from NIR instrument and yield useful analytical information (Blanco and Villarroya, 2002; Osborne et al., 1993). However, the data acquired from NIR spectrometer contains background information and noise besides sample information. In order to obtain reliable, accurate and stable calibration models, it is necessary to pre-process spectral data before modeling (Cen and He, 2007). Spectral preprocessing techniques are required to remove any irrelevant information including noise.
uncertainties, variability, interaction and unrecognized features. Determining of pre-treatment method to develop calibration model NIR depends on material type and content to be predicted (Mouazzen et al., 2005).

**Calibration model**

Calibration model was established using PLS algorithm. Statistical parameters used to evaluate the developed NIR calibration models were:

1) **Bias**, i.e., the average deviation between the reference value \(x_n\) and the predicted value \(y_n\) of V-Set. It is recommended that Bias should equal to zero (Williams and Norris, 1990).

\[
Bias = \frac{1}{n} \sum (x_n - y_n)
\]

2) The standard error of calibration set (SEC), i.e., the standard deviation of the differences between the reference value \(x_n\) and the predicted value \(y_n\) of C-Set, corrected for bias.

\[
SEC = \sqrt{\frac{1}{n-1} \sum (x_n - y_n - Bias)^2}
\]

3) The standard error of validation set (SEP), i.e., the standard deviation of the differences between the reference value \(x_n\) and the predicted value \(y_n\) of V-Set, corrected for bias.

\[
SEP = \sqrt{\frac{1}{n-1} \sum (x_n - y_n - Bias)^2}
\]

4) Coefficient of corelation \(r\) between the reference value \(x_n\) and the predicted value \(y_n\).

\[
r = \frac{\sum (x_n-x_{\bar{n}})(y_n-y_{\bar{n}})}{\sqrt{\sum (x_n-x_{\bar{n}})^2} \sqrt{\sum (y_n-y_{\bar{n}})^2}}
\]

The model is considered more useful when \(r\) value approaches 1, whereby \(r\) value is larger than 0.90, considered as high correlation (Williams and Norris, 1990).

5) Coefficient of determination \(R^2\) between the reference value \(x_n\) and the predicted value \(y_n\).

\[
R^2 = \left( \frac{\sum (x_n-x_{\bar{n}})(y_n-y_{\bar{n}})}{\sqrt{\sum (x_n-x_{\bar{n}})^2} \sqrt{\sum (y_n-y_{\bar{n}})^2}} \right)^2
\]

6) Coefficient of variation (CV);

\[CV\text{ in } C\text{-Set: } CV = \frac{SEC}{\bar{x}} \times 100\]

\[CV\text{ in } V\text{-Set: } CV = \frac{SEP}{\bar{x}} \times 100\]

A very reliable calibration could be achieved when the value of CV in C-Set was lower than 5\% and the value of CV in V-Set was lower than 10\% (Mlček et al., 2006).
Results and discussion

NIR Spectra Analysis

References data of SSC, pH and firmness in sample of mango fruits for calibration set and validation set are shown on Table 1.

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<th>Minimum</th>
<th>Maximum</th>
<th>Mean</th>
<th>SD</th>
</tr>
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<tr>
<td><strong>SSC(°Brix)</strong></td>
<td></td>
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<tr>
<td>Calibration</td>
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<td>21.07</td>
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<td>3.12</td>
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<tr>
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<td>21.07</td>
<td>16.33</td>
<td>3.23</td>
</tr>
<tr>
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<tr>
<td>Calibration</td>
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<td>1.62</td>
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<tr>
<td>Validation</td>
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<td>0.28</td>
<td>3.93</td>
<td>1.30</td>
<td>1.57</td>
</tr>
</tbody>
</table>

*Number of samples

Figure 1 and 2 show original spectra and normalized pre-treatment NIR spectra in mango fruits. The original one shows that there is a parallel shift of spectra. It occurred because spectra data of NIR did not only contain sample information, but also background information as well as noises. Therefore, pre-treatment was needed before modelling to get reliable, accurate and stable calibration model (Cen and H, 2007). Spectra data resulted from diffuse reflectance measurement at solid sample would be followed by scattering noise as a result of particle size difference (Chen et al., 2013). This case was supported by Blanco and Villarroya (2012) who acknowledged that physical properties of solid samples influence spectra of solid samples. Spectra pattern of near infrared reflectance indicated that wavelength of 1215-1395 nm was CH₂, 1450 nm and 1940 nm were water, 1765 nm was CH₂ and cellulose, and 2252-2400 was carbohydrate.
Figure 1. Original reflectance NIR spectra of mango fruits

Figure 2. Normalized reflectance NIR spectra of mango fruits
Calibration model

Calibration and validation of NIR spectra were carried out to predict SSC, pH and firmness of mango fruits. Calibration was obtained based on the correlation between data of NIR reflectance with SSC, pH and firmness (Table 2). For calibration set, it was obtained that Bias, SEC, CV and R² for SSC, -0.004, 0.15707, 4.35 and 0.884 for pH, -0.048, 0.63, 38.55 and 0.787 for firmness, respectively. For prediction set, it was obtained for Bias, SEP, CV and R² were 0.2604, 2.64867, 16.22 and 0.39 for SSC, -0.0006, 0.17512, 4.87 and 0.87 for pH, 0.0094, 0.69, 43.84 and 0.75 for firmness, respectively. The result showed that the model has a good correlation. This value was good as Mouazen et al. (2005) stated that calibration model having value of R² between 0.66 and 0.81 indicated approximate quantitative predictions, between 0.82 and 0.90 was considered to be a good prediction, and larger than 0.91 revealed excellent.

SEC and SEP value in this study has a quite small. This result was good since there was a small difference between SEC and SEP values. Good calibration model has a small difference between SEC and SEP. A large difference is an indication of calibration set of not a representative of validation set (Lammertyn et al., 2000). When SEP value is larger than two times than SEC, most likely over fitting will occur (Hruschka, 1990). SEP values of this study were smaller than SEC, which led to prevent the over fitting.

Figure 3, 4 and 5 show data distribution of calibration and prediction of SSC, pH and firmness. The r value indicates that PLS was an appropriate calibration technique to extract spectra variation relate to SSC, pH and firmness of mango fruits. Bias value at set calibration for SSC, pH and firmness of this study were 0.230, -0.004 and -0.048, respectively. When the evaluation was conducted using new sample at set validation. Bias value for SSC, pH and firmness were 0.2604, -0.0006 and 0.0094, respectively. It showed that accuracy of calibration could be maintained to predict SSC, pH and firmness.

Table 2. Calibration and validation of NIR model for SSC, pH and firmness

<table>
<thead>
<tr>
<th>SSC (°Brix)</th>
<th>Calibration</th>
<th>Validation</th>
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</thead>
<tbody>
<tr>
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<tr>
<td>CV (%)</td>
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<tr>
<td>R²</td>
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<table>
<thead>
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<th>pH</th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>N*</td>
<td>103</td>
<td>N*</td>
</tr>
<tr>
<td>Bias</td>
<td>-0.004</td>
<td>Bias</td>
</tr>
<tr>
<td>SEC</td>
<td>0.15707</td>
<td>SEC</td>
</tr>
<tr>
<td>CV (%)</td>
<td>4.35</td>
<td>CV (%)</td>
</tr>
<tr>
<td>R²</td>
<td>0.884</td>
<td>R²</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Firmness (kgf)</th>
<th>Calibration</th>
<th>Validation</th>
</tr>
</thead>
<tbody>
<tr>
<td>N*</td>
<td>103</td>
<td>N*</td>
</tr>
<tr>
<td>Bias</td>
<td>-0.048</td>
<td>Bias</td>
</tr>
<tr>
<td>SEC</td>
<td>0.63</td>
<td>SEC</td>
</tr>
<tr>
<td>CV (%)</td>
<td>38.55</td>
<td>CV (%)</td>
</tr>
<tr>
<td>R²</td>
<td>0.787</td>
<td>R²</td>
</tr>
</tbody>
</table>

N*: number of samples

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Figure 3. Measured SSC by reference method and predicted SSC by NIR

Figure 4. Measured pH by reference method and predicted pH by NIR

Figure 5. Measured firmness by reference method and predicted firmness by NIR
Conclusion

This study has established a technique, based on NIR spectroscopy of the fruit, for predicting the ripe-stage qualities i.e. SSC, pH and firmness of mango fruits cv Gedong Gincu. By means of partial least square (PLS) regression relationship was established between reflectance spectra and SSC, pH and firmness parameters. PLS method resulted good calibration results for SSC, pH and firmness prediction. The predicted values were highly correlated with destructively measured values. It was concluded that by using the NIR spectroscopy measurement system, in the appropriate spectral range, it is possible to nondestructively predict the SSC, pH and firmness of mango fruit.

Acknowledgement

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References


