Prediction of hardness development in mangosteen peel using NIR spectroscopy during low temperature storage

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1. Introduction

Mangosteen is a famous exotic, tropical fruit, sometimes called the queen of fruits. Mangosteen is usually consumed when fully ripe, but still fresh. It has an attractive appearance: green calyx, a thick red to purple colored peel, and white edible tissue. In addition it has a bracing taste, with a combination of sweet and sour taste. It has an attractive appearance: green calyx, a thick red to purple colored peel, and white edible tissue. In addition, it has a bracing taste, with a combination of sweet and sour taste.

Mangosteen is a major fruit export of Indonesia, about 34% of the total fruit export from Indonesian. Among the countries mangosteen is exported to are Singapore, China, Hong Kong, Taiwan, and some countries in the Middle East, such as United Arab Emirates and Saudi Arabia. In 2009, export volume from Indonesia was 4285 tons, worth USD 2,781,712. In 2010, the export volume increased to 8225 ton, worth USD 6,310,272 (BPS, 2011).

Regional variations in mangosteen quality are a major concern for exporters in Indonesia. This poor quality mangosteen can be caused by improper harvest time, yellow latex deposits, broken calyxes, stem and peel bruising, and peel hardening, especially when fruit are stored at low temperatures for a long period.

Peel hardening results in a hard outer skin that is difficult to peel and disliked by consumers, and is said to be related to the water content of the peel pulp itself. Previous research shows that peel pulp hardening is a function of decreasing water content during low temperature storage, as a result of transpiration and respiration processes (Suyanti and Setyadji, 2007). Careful observations of the peel pulp of mangosteen reveal that at the beginning of storage inter cellular spaces in the parenchyma tissue contain water. As this water evaporates during storage, the cell wall becomes thicker and harder. Loss of water from the parenchyma tissue and thickening of the cell walls result in peel hardening, as cells shrink and compact together (Qanytah, 2004).

Traditional methods of measuring water content of the peel pulp of mangosteen are destructive in nature, and thus the same fruit cannot be continually monitored. While NIR spectroscopy cannot directly measure peel hardness of fruit, it can be used for nondestructive measurement of fruit components, such as water content, protein, carbohydrate, and fat (Pasquini, 2003). The...
measurements are fast, highly precise, need no special sample pretreatment, or chemical additives; thus there is zero waste (Osborne et al., 1993). Examples of the application of NIR spectroscopy to the measurement of moisture content, include several types of grains (Nicolai et al., 2007), fish oil (Cuzzolino et al., 2005), surimi (Uddin et al., 2006), and Mafazati dates (Mireei et al., 2010).

The objectives of this research are to develop a NIR spectroscopy calibration model to predict moisture content in mangosteen peel during low temperature storage, and then to relate this measurement to hardness development in mangosteen.

2. Methodology

2.1. Materials and equipment

Fresh mangosteens were obtained from a farmer in Purwakarta, West Java, Indonesia. The fruits were harvested at a level 2 ripening index, which is when the fruits are turning red color, and weight about 80–100 g each. Experiments were conducted in two stages. At each stage of the experiment fruits were obtained from a single location. The second experiment was conducted one month after the first experiment. Theobendazole (TBZ) was used to prevent fungal attack during storage. A NIRFlex N-500 fiber optic solids spectrometer with a gun type probe was used to measure the reflectance of the fruit between 900 and 2500 nm. Other equipments used included a high precision digital scale, constant temperature oven, digital rheometer, refrigerator, desiccator, cutter, washbasin, fruit crate, and aluminum foil.

2.2. Procedures for first step experiment

In the first experiment an NIR calibration model was developed to predict moisture content in mangosteen peel, as well as determine the relationship between moisture content and peel hardness through destructive measurements. At each low temperature storage condition (8 °C and 13 °C), 64 fruits were stored, while at room temperature (ca. 27 °C), 104 fruits were stored. For those stored at 8 °C and 13 °C, the NIR reflectance measurements were conducted on day 0, 1, 2, 4, 8, 16, 24, and 28, while for those stored at room temperature, the reflectance measurements were conducted on day 0, 1, 2, 3, 4, 5, 6, 7, 8, 10, 12, 14, and 16. At each measurement 8 NIR reflectance scans of the fruit were captured, and then hardness and moisture content of the peel were destructively measured. Measurement of NIR reflectance, hardness, and moisture content were conducted at three different positions along a transect (near the top, middle, and near the bottom) of each fruit, and then the three measurements at each position were averaged.

The NIR reflectance of the peel was measured from 1000 to 2500 nm at 0.4 nm intervals. Hardness was measured using a Sun Rheonmeter CR-300 type with a 2.5 mm plunger diameter, until the plunger penetrated to a depth of 4 mm, with a rate of penetration of 60 mm/min. Subsequent analysis of the hardness results used the average value of the three replicate measurements. Moisture content (MC) of the peel was determined by oven drying at 105 °C, until a constant weight had been reached, for each fruit at the three locations (2 x 2 x 0.4 cm³) where the NIR reflectance measurements had been taken. An averaged MC value for each of the positions was used in subsequent analysis.

For calibration and validation, a partial least square (PLS) method was used, where the NIR reflectance data were divided into two groups, one for calibration and the other for validation. Two thirds of the data set was used for calibration and one third for validation at each storage condition tested. Pre-treatment of the data prior to the calibration process was performed by normalization of the data into a 0–1 range.

The results of the calibration and validation were evaluated based on the correlation coefficient (R), root mean square error (RMSE), and coefficient of variation (CV). RMSE for the calibration group is referred to as RMSEC, and for the validation group as RMSEP. To calculate the proportional error level, RMSEP was compared with the value of CV. A good calibration model will have a high value of R, a low CV, and RMSEC and RMSEP values that are almost the same (William and Norris, 1990). In this experiment, a calibration model is considered to be good if R > 0.75 and CV < 5% (Pasquini, 2003). The best calibration model was then used to predict moisture content of fruit peel in the next step of the experiment.

The relationship between moisture content and peel hardness was determined by regression analysis. Testing for normality of residual distribution was performed using a Kolmogorov–Smirnov test prior to data analysis. Residual data is considered to be distributed normally if the p-value > 5%. For the regression equation, it can be used only if the p-value < 5% after analysis of variance (ANOVA), the resulting equation was used to predict peel hardness from changes in moisture content in the next step of the experiment.

2.3. Procedures for second step in the experiment

The objective of the second step of the experiment is to determine the pattern of hardness increase, based on changes in moisture content. For this purpose, ten mangosteen samples were stored at both 8 °C and 13 °C for 28 days, as well as another ten fruit were stored at room temperature for 16 days. The NIR reflectance of all the fruit stored at 8 °C and 13 °C were measured on day 0, 2, 4, 8, 16, 24 and 28, and on day-0, 2, 4, 6, 8,10,12,14, and 16 for the fruit stored at room temperature. The NIR reflectance data at each storage temperature were normalized to 0–1, and then were used to predict moisture content of fruit peel using the best calibration model obtained in the first step of the experiment. This was used to determine moisture content change during storage.

This data set on moisture content of peel during storage was then used to predict the hardness of the peel, using the regression equation obtained during the first step of the experiment. Hardness was predicted for all three storage temperatures. As in the first experiment, testing for normality of residual distribution was performed using a Kolmogorov–Smirnov test prior to data analysis. Residual data is considered to be distributed normally if p-value > 5%. The regression equation, was only used if a p-value < 5% was obtained after analysis of variance (ANOVA).

3. Results and discussion

3.1. Change of mangosteen quality during storage

Three quality parameters of mangosteen were observed to deteriorate during storage at all three temperatures. The first parameter was the appearance of a yellow latex on the inner surface of the peel that contaminated the flesh. This was observed in about 3% of the 232 samples. The second parameter was the appearance of black spots on the surface of the peel from day-20 right through to the end of storage. The third parameter was a change in fruit flesh color, from a white to gray color. And in some of the samples fungal rots were observed.

This quality deterioration commenced at increasingly shorter storage times: day-28, 24, and 14 for samples stored at 8 °C, 13 °C, and room temperature respectively. This occurred in 37.5%, 25%, and 12.5% of the fruit stored at the respective temperatures.
shelf-life of the mangosteen stored at 13 °C and 8 °C was 28 days, while for those stored at room temperature was 16 days. The damaged fruit tended to have harder peel than undamaged ones, so these damaged fruit were not included in hardness measurements.

3.2. Change of moisture content and hardness during storage

Mangosteen peel moisture content generally decreased during storage at all temperatures measured. The highest decrease was in those fruit stored at room temperature, 6.9% after 16 days storage, while the lowest was for those fruit stored at 8 °C: 2.8% after 28 days storage. The rate of decrease in moisture content during storage was 0.066%, 0.281%, and 0.459% per day at 8 °C, 13 °C, and room temperature storage conditions respectively (Fig. 1). While moisture content consistently decreased during the entire storage period, peel hardness initially decreased and then began to increase until the end of storage at all temperatures measured. This initial decrease in hardness occurred up until day-16 for those fruit stored at 8 °C and 13 °C, and until day-7 for those fruit stored at room temperature.

3.3. Analysis of NIR reflectance

Generally, the fruit peel NIR reflectance between 1000 and 2500 nm was the same for all fruit measured (Fig. 2), except for those fruit stored at 8 °C, which had a wider distribution compared to those stored at the other two temperatures.

Data pretreatment by normalization into a 0–1 range was necessary in order to decrease the error value due to differences in particle size and the range of reflectance values. After normalization, the reflectance data were transformed into absorbance log [1/reflectance]. In the absorbance spectrum of mangosteen peel, absorption peaks were located at 1190, 1450, and 1940 nm. These are associated with the O–H energy absorption band in the water molecule, i.e., moisture content. Absorption peaks were also located between 1765 and 1780 nm, which reflect CH2 and cellulose, as well as absorption peaks above 2400 nm, which reflect carbohydrate content (Osborne et al., 1993).

Calibration and validation models, based on the correlation between NIR data and destructively determined moisture content, were used to predict moisture content of mangosteen peel. The calibration and validation models were developed using the PLS method. The data used in this analysis was from those fruit which were still in good (quality) condition, i.e., those acceptable to consumers. The total number of fruit stored was 192, 192, and 312 at 8 °C, 13 °C, and room temperature, respectively. Two-thirds (2/3) of the data set was used for calibration, and the remaining third (1/3) used for validation. Descriptive water content values for the data set are shown in Table 1.

The result of moisture content calibration of mangosteen stored at had a correlation (R) of 0.758, 0.861, and 0.822. stored at 8 °C, 13 °C, and room temperature, respectively (Fig. 3). These correlation values indicate that moisture content partially contributes to the NIR spectra, to varying degrees, at all storage temperatures. These results also indicate that fruit stored at higher temperatures experienced a higher rate of water lost. Thus, NIR spectroscopy can be used to better predict hardness at these higher temperatures.

The calibrations performed as follows; RMSEC and RMSEP varied between 0.09 and 0.39%, and CV values between 2.5 and 3.3%. These indicate that the model is accurate and stable (Table 2). In other words, the NIR calibration using the PLS method can be used to predict moisture content of mangosteen peel during storage. The moisture content, as determined by NIR, is associated with the O–H bonds, with absorbance peaks clearly seen at 1190 nm, 1450 nm, and 1940 nm.

3.4. Prediction of peel hardness through moisture content

A correlation between moisture content and peel hardness was obtained using nonlinear regression, except for fruit stored at 8 °C because of the very small change in moisture content in the samples at this temperature. Hardness tends to decrease at the
beginning of storage, and increased from the middle until the end of the storage period. Moisture content consistently decreased over the stored period (Fig. 4).

ANOVA of the regression for fruit stored at 8°C had a p-value >5%, i.e., the model did not predict moisture content very well. At 8°C, the range in moisture content for sampled mangosteen peel was only 63.03–65.52% and hardness values ranged from 3.14 to 5.04 N. This narrow range of moisture content means that correlations between moisture content and peel hardness were not good. Meanwhile, at 13°C and room temperature storage, a wider range of mangosteen peel moisture content data was obtained. The moisture contents were 56.22–64.84% and 58.25–65.13% for samples stored at 13°C and room temperature, respectively. The peel hardness ranged from 2.43 to 5.17 N and 1.78–3.73 N for samples stored at 13°C and room temperature, respectively. The relationship of moisture content and peel hardness for the samples stored at 13°C was $$y = 0.0797x^2 - 9.833x + 305.9$$, and for the samples stored at room temperature was $$y = 0.1208x^2 - 14.90x + 461.16$$, where x is moisture content and y is peel hardness. It should be noted that it is thought that other factors also contribute to changes in peel hardness during storage, although these have yet to be determined.

The moisture content of ten samples was monitored continuously during storage (at all three temperatures) using the NIR method. At all three storage temperatures there was a similar decrease in moisture content as a function of storage time. As expected, the highest and lowest rates of decrease were observed for samples stored at room temperature and 8°C, respectively (Fig. 4).

In general, NIR prediction values for peel moisture content decreased linearly with storage time for all three storage temperatures. The highest being 5.85% after 16 days storage at room temperature, and the lowest being 1.99% after 28 days storage at 8°C. The rate of moisture content decrease was 0.057%, 0.253%, and 0.421% per day for samples stored at 8°C, 13°C, and room temperature, respectively. Based on the $$R^2$$ value, the contribution of storage time to decreases in moisture content ranged from 84.0 to 96.3%.

These moisture contents, as determined by NIR, of the ten monitored samples were then used to calculate peel hardness, as shown in Fig. 5. As the samples stored at 8°C suffered chilling injury, which was only discovered at the end of the storage, they have not been included in the analysis. The regression analysis for predicted moisture content and calculated peel hardness were nonlinear for both 13°C and room temperature storage. After this, changes in peel hardness were indirectly predicted with moisture content measurements as determined by NIR. While the moisture content decreased continuously during storage, peel hardness initially decreased and then increased after that, for both storage temperatures.

Peel hardness values predicted from mangosteen stored at 13°C remained higher than those stored at room temperature. The

### Table 1

Descriptive moisture content data for calibration and validation of NIR by PLS method.

<table>
<thead>
<tr>
<th>Statistic description</th>
<th>Temp. 8°C</th>
<th>Temp. 13°C</th>
<th>Temp. 27°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. of data</td>
<td>128</td>
<td>64</td>
<td>128</td>
</tr>
<tr>
<td>Min (%)</td>
<td>60.57</td>
<td>61.87</td>
<td>50.79</td>
</tr>
<tr>
<td>Max (%)</td>
<td>68.38</td>
<td>67.10</td>
<td>67.84</td>
</tr>
<tr>
<td>Avg. (%)</td>
<td>64.78</td>
<td>64.58</td>
<td>62.16</td>
</tr>
<tr>
<td>Std. dev. (%)</td>
<td>1.91</td>
<td>1.58</td>
<td>3.90</td>
</tr>
</tbody>
</table>

### Table 2

Parameters of NIR model calibration and validation for moisture content in mangosteen peel.

<table>
<thead>
<tr>
<th>Storage temperature</th>
<th>Calibration</th>
<th>Validation</th>
<th>Dif. in RMSE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$R^2$</td>
<td>RMSEC (%)</td>
<td>RMSEP (%)</td>
</tr>
<tr>
<td>8°C</td>
<td>0.758</td>
<td>1.25</td>
<td>1.64</td>
</tr>
<tr>
<td>13°C</td>
<td>0.861</td>
<td>1.98</td>
<td>2.07</td>
</tr>
<tr>
<td>27°C</td>
<td>0.882</td>
<td>1.73</td>
<td>1.87</td>
</tr>
</tbody>
</table>

Fig. 3. Result of MC calibration 8°C (above), 13°C (left-below), and room temperature (right-below).

Fig. 4. Regression analysis of moisture content and peel hardness (above) and change in average peel moisture content as the results of NIR prediction (below).
observed peel hardness varied from 2.73 to 3.64 N and 1.56–2.69 N, based on 58.30–65.30% and 58.83–64.69% moisture content, as determined by the NIR method, for samples stored at 13 °C and room temperature, respectively. Mangosteen stored at a lower temperature tended to have a harder peel and are more sensitive to chilling injury (Andgcham et al., 2008).

3.5. Peel hardness development in storage, as predicted by NIR reflectance

Regression analysis showed peel hardness changed non-linearly during storage, initially decreasing and then increasing after that. The decrease in peel hardness at the beginning of storage is thought to be due to non-soluble proto-pectin degradation into pectic acid and pectin which are water-soluble (Winarno, 2002). The process is known as fruit ripening, or at least happens during the fruit ripening process where carbohydrates are broken down into sugars. At higher storage temperatures, the change in peel hardness is faster. Based on changes in peel hardness, the fruit became ripe after 12–16 and 6–8 days of storage at 13 °C and room temperature, respectively. During these periods, peel hardness decreases as the fruit ripen. The change in peel hardness, based on predicted moisture content can be predicted using the $y = 0.0045x^2 - 0.126x + 3.64$ over 28 days for fruit stored at 13 °C, and $y = 0.0138x^2 - 0.218x + 2.69$ over 16 days for fruit stored at room temperature, where $y$ is hardness in Newton and $x$ is storage period in days. Based on $R^2$ values, the contribution of storage period to peel hardness varied from 70.1% to 87.4%.

4. Summary and conclusions

1. NIR reflectance was used to predict moisture content of mangosteen peel during storage at 8 °C, 13 °C, and room temperature.
2. Peel hardness of mangosteen can be predicted based on predicted moisture content for mangosteen stored at 13 °C and at room temperature, but not for mangosteen stored at 8 °C.
3. The pattern of peel hardness change, based on changes in NIR reflectance determined moisture content predicted using the equation $y = 0.0045x^2 - 0.126x + 3.64$ ($R^2 = 0.874$) over 28 days for fruit stored at 13 °C, and $y = 0.0138x^2 - 0.218x + 2.69$ ($R^2 = 0.701$) over 16 days for fruit stored at room temperature.

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References

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