Non-destructive determination of the main chemical components of red dragon fruit peel flour by using Near-Infrared Reflectance Spectroscopy (NIRS)

Y Hotmaida¹ and Sutrisno²

¹Department of Mechanical and Biosystem Engineering, IPB University, Indonesia
²Corresponding author, Email: trisno406@apps.ipb.ac.id

Abstract. Red dragon fruit peel is still not optimally utilized and only becomes waste. According to previous research, it is known that red dragon fruit peel contains 72.1% carbohydrate, 0.7% fat, 3.2% protein, and 46.7% food fiber and contains betacyanin of 186.90 mg / 100g dry weight and 53.71% antioxidant. One of the solutions to use red dragon fruit peel is to process it into flour. The accurate and efficient determination of the chemical content of red dragon fruit peel flour can be realized through the development of the Near-Infrared Reflectance Spectroscopy (NIRS) technology. The sample that used was made directly from the waste of red dragon fruit peel with a process of flouring, then measured the spectra with NIRS and the chemical content of the sample destructively. The reflectance spectra as output were transformed into absorbance spectra. Data calibration uses a partial least squares (PLS) method with several variations in the number of factors and pretreatment data in the form of normalization and smoothing Savitzky-Golay smoothing (SGs), resulting in the best calibration regression model in estimating water, ash, carbohydrate, and protein content. In contrast, the estimation of fat cannot be done non-destructively by using the NIRS method.

1. Introduction
One type of fruit that is the result of Indonesian agricultural production is the red dragon fruit (Hylocereus polyrhizus), which is also often referred to as the pitaya. In Indonesia, the flesh of the fruit is widely consumed by being eaten directly or processed into other foods and drinks. The demand for dragon fruit production has increased every year, especially the Chinese new year celebration, where the demand for these fruits can reach 30–40% of annual production [1]. The increased consumption of dragon fruit has an impact on the rest of the peel that is just thrown away. The peels of dragon fruit account for 30–35% of the whole fruit and are usually only a waste. Based on these contents, one way to increase the economic value of the red dragon fruit peel is to use it in the form of flour. The utilization of red dragon fruit peels in the form of flour is expected to help reduce the use of wheat flour that must still be imported to Indonesia to meet the production of flour.

Based on previous research, it is known that dragon fruit peel flour contains main chemical components that are not much different from wheat flour; besides that, there is also a natural dye in dragon fruit peel flour, which is not owned by wheat flour. Thus, the dragon fruit peel flour can be used as a substitute for wheat flour, especially in its use as food ingredients. Of course, before it can be
consumed, the dragon fruit peel flour must go through several tests to ensure the quality and eligibility as food ingredients or products. The tests usually still use conventional methods, which require a long time, quite complex stages, relatively expensive costs, complete and adequate laboratory equipment, and experts. Therefore, methods and technologies that are easier, cheaper, faster, precise, accurate, and without having to damage the material are needed to test the estimated content or chemical component of a material which, in this case, is for the dragon fruit peel flour itself.

The use of near-infrared reflectance spectroscopy (NIRS) is one of the methods that can be used. By using the NIRS method can analyze at high speed, does not cause pollution, does not use chemicals, and does not damage (non-destructive). The use of the NIRS method in testing the chemical content of several types of starch has previously been carried out, such as estimating the water content, carbohydrates, protein, and corn flour fat [2]. It has also can be used to estimate the chemical composition of MOCAF flour [3] and to estimate the main chemical content of wheat flour [4]. Based on this, the NIRS also can be applied as one of the methods in determining the main chemical components of the red dragon fruit peel flour without destructively.

2. Materials and methods

2.1. Materials and tools

The material used in this study was red dragon fruit peel waste obtained from fruit juice shops and even from the red dragon fruit consumption by personal and people around, then made into flour through a process of flouring and size reduction. Dragon fruit peel flour needed for each sample is 25 grams with the number of samples for calibration and validation were 2/3 and 1/3 of the total sample, where the total sample used was 40 samples.

Tools used in this study were electric ovens to measure water content and reduce the water content in making flour, NIRFlex N-500 Fiber Optics Solids Petri SpectrosBuchi brand, computer to process measurement data and software built-in namely CAMO Unscambler X 10.4, other equipment in the form of digital balance Mettler PM 4800 brand and Excellent brand, Adventurer brand Ohaus balance, aluminum cup, desiccator, grinder and sieve with a size of 60 mesh for the reduction in size.

2.2. Sample Preparation

The total number of samples was 40. The peel of the red dragon fruit that has been cleaned was then cut into smaller sizes and dried using an oven at 60°C for 6–7 hours. After the water content was reduced, the dried dragon fruit peel was mashed with a grinder or hammer mill to turn into a powder. Then the sifting was carried out with 60 mesh sieve to produce fine red dragon fruit peel flour.

2.3. Reflectance Measurement of Red Dragon Fruit Peel Flour Spectrum

The wavelengths used in the Petri NIRFlex N-500 Fiber Solids spectrometer in the sample reflectance measurements were 1000–2500 nm or 4000–10000 cm$^{-1}$ with data intervals of 1 nm or 4 cm$^{-1}$. Spectrum data collection was carried out by giving or firing infrared light (NIR) at samples placed in Petri dishes. Each cup contains 25 grams. Measurements were made at three different points so that the total number of spectra obtained were 120 spectra. The data from the test results were then analyzed using the software Unscrambler.

2.4. Determination of Chemical Content in Conventional (Destructive) Methods

Determination of Water Content

Water content was determined by the thermogravimetric method. First, the empty ceramic cup was dried at 105°C for 15 minutes, then cooled in a desiccator for 10 minutes, and then weighed the mass of the cup. Two grams of the powdered sample was put in the cup and then dried in the oven at 105°C for 8 hours. The cup was removed from the oven and then cooled and weighed again. The weight of the sample before roasting (A) was the total weight (flour of dragon fruit peel and cup) minus the weight of
the cup. The weight of the sample after roasting (B) was measured in the same manner. The water content can be calculated by equation 1.

\[
\text{Water Content (\%w.b.)} = \frac{A - B}{A} \times 100\% 
\]

(1)

**Determination of Ash Content**

Determination of ash content was done by first drying the cup used in the oven for 15 minutes, then cooled into a desiccator, and weighed (A). Next, weigh the powdered sample as much as 2 grams in a cup (B) and burn in the smoke chamber to obtain ash or until the weight is constant. Ignition carried out in an electric furnace was carried out at a temperature of 400–600 °C for 4-6 hours. The results of the graying with the plates were then cooled and weighed (C). The amount of ash contained in the sample was calculated using equation 2.

\[
\text{Ash Content (\%w.b.)} = \frac{C - A}{B} \times 100\%
\]

(2)

**Determination of Protein Content**

Protein content was determined using the Kjeldahl method. Briefly, ca. 100 mg of the powdered sample was put into a 30 ml Kjeldahl flask with 1.9±0.1 g K$_2$SO$_4$, 40±10 mg HgO, and 3.8±0.1 ml H$_2$SO$_4$, and then boiled for 1-1.5 hours until the liquid becomes clear. After the distillation and titration process with 0.02 N HCl solution, the protein content was calculated by equations 3 and 4.

\[
N(\%) = \frac{((\text{ml HCl sample} - \text{ml blank}) \times \text{N HCl} \times 14.007 \times 100\%)}{\text{mg sample}}
\]

(3)

\[
\text{Protein Content (\% w.b.)} = \%N \times 6.25
\]

(4)

**Determination of Fat Content**

Two grams of the powdered sample was spread on cotton cloth with filtered paper and rolled to form a thimble, then put into soxhlet extractor. The extraction was carried out for 6 hours with 150 ml of hexane. The extracted fat was then dried in an oven at 100°C for 1 hour. Fat content was computed using equation 5.

\[
\text{Fat Content (\%)} = \frac{\text{Extracted fat weight}}{\text{Sample weight}} \times 100
\]

(5)

**Determination of Carbohydrate Content**

Carbohydrate Content (\%) = 100\% - (water + ash + protein + fat)

(6)

2.5. Spectrum Data Processing

The spectral data were preprocessed using the help of CAMO Unscambler X 10.4. Preprocessing used in this study were Normalization (N), Standard Normal Variate (SNV), Multiplicative Scatter Correction (MSC), and Smoothing Savitzky-Golay (SGs).

2.6. Calibration and Validation

The partial least squares (PLS) method was used for determining the relationship between the chemical content of dragon fruit peel flour and NIR absorbance. The calibration model was evaluated using statistical parameters including Standard Error of Calibration set (SEC), Standard Error of Validation set (SEP), correlation coefficient (R), a ratio of prediction to standard deviation (RPD), coefficient of variation (CV), bias, and a ratio of SEC to SEP (consistency).
3. Result and Discussion

3.1. Chemical Contents of Red Dragon Fruit Peel Flour
The chemical content of red dragon fruit peel flour consists of water, ash, protein, fat, and carbohydrate content. Table 1 shows the chemical compositions in the powdered samples.

| Chemical Content | Average | Standard Deviation | Maximum | Minimum |
|------------------|---------|---------------------|---------|---------|
| Water (%)        | 6.73    | 0.68                | 8.58    | 5.37    |
| Ash (%)          | 18.51   | 1.40                | 21.66   | 15.03   |
| Protein (%)      | 6.38    | 1.50                | 9.27    | 3.44    |
| Fat (%)          | 0.77    | 0.24                | 1.66    | 0.40    |
| Carbohydrate (%) | 67.70   | 2.36                | 72.72   | 64.14   |

A high standard deviation indicates that a material has a high diversity value. Carbohydrates have the highest standard deviation values among other chemical contents. However, from the percentage point of view, carbohydrate has the lowest standard deviation. Different from the other flour (such as wheat of MOCAF flour), dragon fruit peel flour has a high ash content. Ash content itself is related to the mineral content of an ingredient. If the water evaporates during the drying process very much, it causes more minerals to be left behind and ash levels to increase [5]. Based on this, the ash content in dragon fruit peel flour is influenced by the drying process carried out.

3.2. Characteristics of the NIR (Near-infrared) Spectrum of Dragon Fruit Peel Flour
Figure 1 shows the absorbance spectrum curve of dragon fruit peel flour. Generally, the spectra collected from intact dragon fruits peel flour had a quite similar pattern with other spectra of other flours. Obvious peaks in wavelengths were found at around 1197, 1480, 1947, 2126, and 2383 nm for fat, protein, water, ash, and carbohydrate, respectively. Table 2 shows the comparison between the wavelengths of the chemical contents of the test results with the reference that can be seen that there are several shifts in each chemical content.

![Figure 1. The absorbance spectrum of red dragon fruit peel flour](image)
Table 2. Comparison of assigned wavelengths of chemical components with previous studies

| Chemical Content | Result | Reference I | Reference II | Reference III |
|------------------|--------|-------------|--------------|---------------|
| Water            | 1947   | 1941        | 1968         | 1940 and 1200 |
| Ash              | 2126   | 1222        | 1483         | 1000 and 1180 |
| Protein          | 1480   | 2115        | 1510         | -             |
| Fat              | 1197   | -           | 1215         | -             |
| Carbohydrate     | 2383   | -           | 1429         | 2280 and 2320 |

As shown in table 2, the reference I is the result of estimating the chemical content of wheat flour, namely water content, ash content, and protein. Reference II is the result of estimating the chemical content of Bondowoso coffee beans consisting of water content, ash content, protein, fat, and carbohydrates, while reference III is the result of estimating the chemical content of MOCAF flour namely, water content, ash content, and carbohydrate. The test results are similar to the reference II, except for ash and carbohydrate content, there is quite a significant difference, whereas when compared with all references ash content has the most different wavelength values. That is because the ash content in the material has a high enough content after carbohydrates, so the resulting wavelength is also quite large.

The absorbance spectrum data produced still has noise and the calibration regression equation model that was built still not good enough. Therefore, the data treatment process in the calibration regression equation was needed to estimate the chemical content of red dragon fruit peel flour. The noise will disrupt the quality of information on spectrum relevance attributes.

3.3. NIR Calibration Results and Validation of Red Dragon Fruit Peel Flour Spectroscopy

The results of PLS regression for each chemical content of red dragon fruit peel flour can be seen in table 3 to table 7.

Table 3 shows the results of the analysis of the estimation of the water content of red dragon fruit peel flour. The best data treatment for estimating water content is the normalization with a factor of 6. The resulting model has a value of \( r = 0.85 \), \( \text{SEC} = 0.35 \), \( \text{SEP} = 0.41 \), \( \text{CV} = 5.95\% \), \( \text{RPD} = 1.63 \) and consistency = 84.11%.

| Pretreatment | Factor of PLS | \( r^2 \) | \( r \) | SEC | SEP | CV (%) | RPD | Consistency (%) |
|--------------|---------------|----------|-------|-----|-----|--------|-----|-----------------|
| Original     | 9             | 0.78     | 0.88  | 0.31| 0.44| 6.28   | 1.55| 70.67           |
| Normalize    | 6             | 0.72     | **0.85** | **0.35** | **0.41** | **5.95** | **1.63** | **84.11** |
| SNV          | 11            | 0.91     | 0.95  | 0.20| 0.50| 7.25   | 1.34| 39.75           |
| MSC          | 10            | 0.85     | 0.92  | 0.25| 0.56| 8.11   | 1.20| 44.99           |
| SGs          | 9             | 0.78     | 0.88  | 0.31| 0.43| 6.18   | 1.57| 72.13           |

The predicted model with normalization was found to have an adequate performance because the consistency value was between 80-110% so that the model is not overfitting [6]. The model with RPD between 1.5–2.0 can be used for rough prediction [7]. The value of the relation coefficient (r) is also satisfactory because it is close to 1, and the SEC and SEP values are adequate because it is close to 0. The value of the CV is almost acceptable because it approaches the value of 5% as the ideal allowable limit. The results of the treatment without pretreatment or with other treatments other than normalization have greater than \( r \) those produced using normalization. However, these treatments have an RPD value...
that is smaller than the normalization and consistency value that is still below 80% so that the model is considered overfitting. The best data distribution of the regression model is shown in figure 2.

![Figure 2](image)

**Figure 2.** Scatter plot of actual against predicted values of water content in red dragon fruit peel flour. The solid line represents the regression line. Diamond and square symbols represent the calibration and validation dataset.

Table 4 shows the estimation of the ash content of red dragon fruit peel. The best data processing are provided by Savitzky-Golay (SGs) smoothing treatment with a factor of 10. The model has a value of $r = 0.90$, SEC = 0.56, SEP = 0.75, CV = 4.13%, RPD = 2.00 and consistency = 75.10%. RPD values between 2.0–2.5 can be used for quantitative predictions [7]. In addition, the value of the relation coefficient ($r$) is also quite good because it is close to 1, and the SEC and SEP values are quite good because it is close to 0. The results of the value of the coefficient of diversity (CV) can be accepted and quite feasible because the allowable ideal limit is 5%. In all prediction models with all treatments, the consistency value is still less than 80%, so that the model is likely to experience overfitting, including the best data processing results by SGs. The statistical parameter values generated in the data without treatment are almost the same as those produced by SGs as the best data processing, but in normal data have a consistency value of 0.03% smaller than SGs. Meanwhile, data processing other than SGs and without treatment results in $r$ values greater than both but has a smaller RPD value and consistency so that it is not more feasible to use. The best data distribution of the regression model is shown in figure 3.

| Pretreatment | Factor of PLS | $r^2$ | $r$ | SEC | SEP | CV (%) | RPD | Consistency (%) |
|--------------|---------------|------|-----|-----|-----|--------|-----|-----------------|
| Original     | 10            | 0.81 | 0.90| 0.56| 0.75| 4.13   | 2.00| 75.07           |
| Normalize    | 11            | 0.93 | 0.96| 0.35| 0.90| 4.93   | 1.67| 38.96           |
| SNV          | 11            | 0.95 | 0.98| 0.29| 0.86| 4.74   | 1.74| 33.09           |
| MSC          | 11            | 0.94 | 0.97| 0.31| 0.92| 5.08   | 1.62| 33.34           |
| SGs          | 10            | 0.81 | 0.90| 0.56| 0.75| 4.13   | 2.00| 75.10           |
The results of the analysis for protein estimation of red dragon fruit peel flour are shown in table 5. The best result was brought by a normalizing treatment with a factor of 10. The developed model has a value of $r = 0.92$, SEC = 0.57, SEP = 0.71, CV = 11.07%, RPD = 2.03 and consistency = 80.49%. The value of the relation coefficient ($r$) is also good because it is close to 1, and the SEC and SEP values are quite good because it is close to 0. The result of the consistency value is between 80-110% so that the model is not overfitting. In all prediction models with all treatments, it produces a coefficient of diversity (CV) of more than 5% as the ideal limit permitted, but the best data processing results can still be used to predict. In addition, based on the above table, it can also be seen that the largest value of $r$ is obtained by using MSC treatment, but has an RPD value that is smaller than normalization and the lowest consistency value among all treatments. Likewise, the treatment with SGs produces the greatest consistency value but has a smaller $r$ and RPD value than normalization. The best data distribution of the regression model is shown in figure 4.

**Table 5. PLSR statistics for protein content**

| Pretreatment | Factor of PLS | $r^2$ | $r$ | SEC | SEP | CV (%) | RPD | Consistency (%) |
|--------------|---------------|-------|-----|-----|-----|--------|-----|-----------------|
| Original     | 11            | 0.84  | 0.91| 0.61| 0.80| 12.37  | 1.82| 76.50           |
| Normalize    | 10            | **0.85** | **0.92** | **0.57** | **0.71** | **11.07** | **2.03** | **80.49**      |
| SNV          | 8             | 0.78  | 0.88| 0.70| 0.85| 13.15  | 1.71| 82.75           |
| MSC          | 15            | 0.97  | 0.99| 0.25| 0.74| 11.49  | 1.95| 34.34           |
| SGs          | 10            | 0.80  | 0.90| 0.67| 0.79| 12.21  | 1.84| 85.12           |

**Figure 3.** Scatter plot of actual against predicted values of ash content in red dragon fruit peel flour. The solid line represents the regression line. Diamond and square symbols represent the calibration and validation dataset.
Figure 4. Scatter plot of actual against predicted values of protein content in red dragon fruit peel flour. The solid line represents the regression line. Diamond and square symbols represent the calibration and validation dataset.

Table 6 shows the results of the fat estimation in red dragon fruit peel flour. The best data treatment for fat estimation is the normalization with a factor of 14. The model has a value of $r = 0.96$, SEC = 0.07, SEP = 0.35, CV = 43.04%, RPD = 0.66 and consistency = 20.43%. Based on the statistical parameter data generated, the prediction model on fat is not suitable to be used because it does not meet the required statistical parameters. The range of chemical content affects the prediction results of NIR. The longer the range, the better the prediction results and vice versa. Judging from the data range of the maximum value with a minimum fat content, i.e., 1.66–0.40, this small range makes the prediction results to be worse. The best data distribution of the regression model is shown in figure 5.

**Table 6. PLSR statistics for fat content**

| Pretreatment | Factor of PLS | $r^2$ | $r$  | SEC  | SEP  | CV (%) | RPD  | Consistency (%) |
|--------------|---------------|-------|------|------|------|--------|------|-----------------|
| Original     | 12            | 0.77  | 0.88 | 0.12 | 0.37 | 46.48  | 0.61 | 31.03           |
| Normalize    | 14            | 0.92  | 0.96 | 0.07 | 0.35 | **43.04** | **0.66** | **20.43**       |
| SNV          | 13            | 0.90  | 0.95 | 0.08 | 0.35 | 43.63  | 0.65 | 22.36           |
| MSC          | 11            | 0.79  | 0.89 | 0.11 | 0.38 | 47.20  | 0.60 | 29.46           |
| SGs          | 15            | 0.90  | 0.95 | 0.08 | 0.36 | 44.63  | 0.63 | 22.04           |
Figure 5. Scatter plot of actual against predicted values of fat in red dragon fruit peel flour. The solid line represents the regression line. Diamond and square symbols represent the calibration and validation dataset.

The results of the carbohydrate estimation of red dragon fruit peel flour are shown in table 7. Savitzky-Golay smoothing (SGs) treatment with a factor of 12 provided the best performance. The model has a value of $r = 0.97$, SEC = 0.58, SEP = 1.37, CV = 2.03%, RPD = 1.74 and consistency = 41.95%. RPD values generated between 1.5 - 2.0, where data can be used to predict. The value of the relation coefficient ($r$) is also very good because it is close to 1, and the SEC and SEP values are quite good because it is close to 0. The results of the value of the coefficient of diversity (CV) is less than 5% as the ideal allowable limit.

| Pretreatment | Factor of PLS | $r^2$ | $r$ | SEC | SEP | CV (%) | RPD | Consistency (%) |
|--------------|---------------|------|-----|-----|-----|-------|-----|----------------|
| Original     | 13            | 0.96 | 0.98 | 0.49 | 1.37 | 2.02  | 1.75 | 35.65          |
| Normalize    | 14            | 0.98 | 0.99 | 0.35 | 1.32 | 1.95  | 1.81 | 26.36          |
| SNV          | 12            | 0.96 | 0.98 | 0.45 | 1.30 | 1.92  | 1.84 | 34.88          |
| MSC          | 13            | 0.97 | 0.98 | 0.43 | 1.38 | 2.04  | 1.73 | 30.80          |
| SGs          | 12            | 0.94 | 0.97 | 0.58 | 1.37 | 2.03  | 1.74 | 41.95          |

All prediction models with all treatments produce a consistency value of less than 80%, so the model is likely to experience overfitting. The largest value of $r$ is generated by using the normalization treatment, and the RPD value is greater than the treatment of SGs. In addition, the largest RPD value is generated by the model with SNV treatment and has a greater $r$-value than the SGs treatment. However, the model produced by SGs has the greatest consistency value among other treatments. So the best treatment is to use SGs. The best data distribution of the regression model is shown in figure 6.
Figure 6. Scatter plot of actual against predicted values of carbohydrate content in red dragon fruit peel flour. The solid line represents the regression line. Diamond and square symbols represent the calibration and validation dataset.

4. Conclusions and suggestions
The non-destructive determination of some of the chemical contents of red dragon fruit peel flour can be done using near-infrared spectroscopy (NIRS). The best calibration model is generated with some variation in the number of factors and pretreatment data in the form of normalization and Savitzky-Golay smoothing (SGs), resulting in the best model in estimating water, ash, carbohydrate, and protein content. Whereas the estimation of fat cannot be done non-destructively by using the NIRS method because the dataset used was not satisfactory enough to meet the required range for developing a model. Data enhancement is needed to improve the accuracy of the estimation model.

References
[1] Heryanto D 2010 Analysis of investment feasibility of the Kusumo agro-tourism dragon fruit business in Kulonprogo Regency (In Indonesian) (Yogyakarta: Graduate School of Gadjah Mada University)
[2] Mala DM 2003 Estimation of water content, carbohydrates, protein, and cornmeal fat (Zea mays) with near-infrared technology (In Indonesian) (Bogor: Graduate School of Bogor Agricultural University).
[3] Purba SF 2010 Estimating the chemical composition of modified cassava flour (MOCAF) by near-infrared (NIR) method (In Indonesian) (Bogor: Graduate School of Bogor Agricultural University).
[4] Novitasari R 2018 Estimation of the main chemical content of wheat flour using near-infrared spectroscopy (In Indonesian) (Bogor: Graduate School of Bogor Agricultural University).
[5] Darmajana AD 2007 Effect of sodium bisulfite concentration on the quality of pineapple core flour (In Indonesian) (Yogyakarta: UGM National Chemical Engineering Seminar) [15] Gabbie NP 2011 Estimation of sorghum seed water, protein and carbohydrate content nondestructively by near-infrared (NIR) method (In Indonesian) (Bogor: Graduate School of Bogor Agricultural University).
[6] Budiastra IW, Sutrisno 2016 Development of methods for determining the chemical quality of Arabica coffee beans that are fast and efficient with near-infrared reflectance spectroscopy (NIRS) to improve the quality and competitiveness of Indonesian coffee National Strategic Research (Bogor: Bogor Agricultural University)
[7] Says W, Mouazen AM, Ramon H 2005 Potential for onsite and online analysis of pig manure using visible and near-infrared reflectance spectroscopy *Biosystems Engineering* 91 (4): 393–402

[8] Lebot V, Champagne A, Malapa R, Shiley D 2009 NIR determination of major constituents in tropical roots and tuber crop flours *Journal of Agricultural and Food Chemistry* 57: 10539-10547