Mathematical Model To Determine Rice Milling Degree Based On Absorbance Characteristic Of Rice Solution At UV Spectrum

Mardison, Sutrisno, Usman Ahmad dan Slamet Widodo

Abstract: Degree of Milling (DM) is an important parameter in determining the quality of milled rice, especially for the graded and labeled rice to put in the market. The development of method to determine the DM quantitatively is very important for checking the quality of rice quickly and accurately before packaging and labeling. This study aims to develop a mathematical model to determine the DM of milled rice based on the absorption characteristics of electromagnetic waves in the UV spectrum by rice solution. The method used in the model development was the empirical approach of the absorbance characteristics of electromagnetic waves in the UV spectrum, resulted from the Ciherang rice in n-Hexane solution. Pre-processing of spectral data by applying smoothing, the first derivative, second derivative and normalization were conducted in the development of mathematical model. It is known that the characteristic of electromagnetic wave absorption in UV spectrum of the rice solution was dominated by 331 nm wavelength. Furthermore, the mathematical model for predicting DM value was developed through the calibration stage and model validation using absorbance data at that wavelength. The calibration stage used the gravimetry method and put as reference to develop the exponential mathematical model with determination coefficient (R^2) of 0.9595, while the determination coefficient for model validation is 0.9504 with Root Mean Square Error of Prediction (RMSEP) of 0.6193.

Index Terms: mathematical model, milling degree, rice, UV absorbance

1 Introduction

RICE (*Oryza sativa*) is a staple food in many countries and almost half the population of the world is consumed in the form of hulled rice (white rice) [16]. In Indonesia, DM is an important parameter in determining the level of quality of rice for industry and consumers. DM is a measure of the extent to which the outer layer of rice (eleurone layer) regardless of brown rice during the milling process. The number of remaining eleurone layers will affect the storage time, quality, and value of the product, because it relates to the appearance and function of end use [6]. Several methods have been developed to determine DM rice such as visual methods, chemical methods and optical methods. Visual inspection is the most common method in the rice milling industry and is also the standard method used by the Federal Grain Inspection Service (FGIS) [6], [13], this method is relatively subjective and depend on the personnel to do it. Color is an important parameter, but can be influenced by other factors besides the rest of the eleurone layer [6]. Chemical methods by using methylene blue have been carried out to determine DM [5], [15], this method is subjective and more time consuming.

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The gravimetric method has been used to determine DM [11], this method is the most appropriate to the meaning of DM itself, but cannot be used to measure DM in blunted rice (rice on the market). Measurement of DM rice on basis of image analysis is dependent on the color of milled rice. More white kernels correspond to higher degree of milling and are measured by pixel determination [14]-[15]. Milling meters using both reflectance and transmittance measurements have been developed. One of such meter has been introduced by Satake (Model MM-liB) on commercial level. This meter analyze the milled rice samples and quantify their DOM on scale of 0-199 [2], [7], this method is only based on the appearance of rice, this does not reflect the true meaning of DM. In addition, this method cannot distinguish between bleached rice and harvested in the rainy season. Chemical methods with methods Surface Lipid Content (SLC) has been used to determine DM [8], although the method is also very good, but this method requires a complex chemical analysis, more time consuming and expensive. Currently, the use of optical-based technology is already very much used to evaluate the quality of agricultural products such as the use of visible and Near Infrared waves Reflectant to determine the physical and chemical properties of rice [12]. Determining the freshness of the rice is also possible using fluorescence imaging with UV light excitation [10]. The development of a new method for the rapid determination of the total concentration of carbohydrates can be accomplised by using UV spectrophotometry [1]. Similarly, use of UV absorption to predict the molar content coefficient of proteins and peptides [3]. The absorbance characteristics based method in the UV spectrum has been successful in analyzing and determining the content of an organic material from agricultural products, so that this method can be used as an alternative in determining DM of rice. This UV absorbance method is very easy in its application, both in preparing samples preparation and the data analyzing. The results of this method can be either a single wavelength or a short range of its, so it is easy to apply to measurement instruments. The measurement of DM of rice using this technology has never been done, so the research to determine DM as one of the parameters of rice quality using UV absorbance is very important. The purpose of this study was to develop a mathematical model to determine the DM of rice based on the characteristics of electromagnetic wave absorption in the UV spectrum.

2 Material and Methods

2.1 Materials

Ciherang variety of rice produced by the Center for Rice Research, Research and Development Ministry of Agriculture, was used as a sample in this study. The sample was cultivated in the Pusakanegara Experimental Garden, Sukamandi, West Java. Ciherang is a type of long-grain rice with high production which is most widely cultivated in Indonesia. The material used is a class of seeds to ensure the purity of varieties with a moisture content of 12-13%. The chemicals used as solvents are n-hexane proAnalysis.

2.2 Instruments

Rice Mill type PAZ-1 DTA, ZACCARIA made in Brazil was used to milling of paddy. The Digital Grain Moisture Meter brand G-WON type GMK303RS was used to measure rice water content. Milling Meter New-MM1D type from Satake-Japan was used to measure milling degree, transparency and whiteness. The Cary 60 UV-Vis UV-Spectrometer type made by Agilent Technologies, Malaysia, was used to obtain absorbance data in the UV spectrum. Cary WinUV software with Scan and Microsoft Excel models was used to process and analyze spectrum data.

2.3 Methods

2.3.1 Sampel Preperation

A total of 120 samples each of 100 g of grain were milled with different DM levels to produce variations in the data with the desired range. The paddy milled to obtain the brown rice and then polished. The difference in the level of milling was done by varying the length of the milling time. The graphimetric method was used as a reference in this study to determine DM. DM can be calculated by the following equation:

$$DM = \left(1 - \frac{W_{milled\ rice}}{W_{brown\ rice}}\right) \times 100\ \% \qquad (1)$$

2.3.2 Absorbance measurement

Absorption measurements in the UV spectrum were carried out on whole milled rice which was dissolved using a solvent with a concentration of 20 ml n-hexane and 10 g of rice (43.3%) with a dissolution time of 2-3 hours. UV absorbance measurements were carried out with a measurement speed of 600 nm / min with a scan module. The measurement results in the form of the characteristic UV absorbance spectrum of rice in the form of absorbance values of wavelengths. UV absorbance measurements were carried out at a wavelength range of 200-400 nm

2.3.3 Pre-treatment of data

Different noise and fluctuation may lead to different interpretation of spectra data, so they need different pre-processing using several data pre-treatment methods prior to spectra characteristic interpretation. Among the data pre-treatment applied in this research were smoothing, first derivative, second derivative [9] and normalization.

2.3.4 Model development

The mathematical model was developed with an empirical approach, where the model was constructed from the results of measurement data in a series of studies. The best correlation between UV absorbance characteristic and DM value was investigated in the wavelength range whit different UV light absorption. The best correlation is expressed with the highest determination value of regression line between UV absorbance and DM of rice. The equation model used in the development of the model was selected based on the unique characteristics of agricultural materials which are usually in exponential form. In addition, the dissolving of fat content on the surface of rice to the inside of rice happens in the form of exponential [4], where in this case the fat content on the surface of rice was used as approach in determining the DM of rice or visual based optics.

2.3.5 Model validation

Validation was done to see the accuracy level of the model, which was stated with a validation error value namely RMSEP, can be calculated by the equation:

$$RMSEP = \sqrt{\frac{1}{n}\sum_{i=1}^{n}\left(Y_i - \hat{Y}_i\right)^2}$$

Where
Yi = ith experimental value
$\hat{Y}_i$ = ith estimated value
N = total number of point to be campared

3 Results and Discussion

The measurement of UV absorbance spectrum was carried out on rice solution as much as 120 samples and the results were presented in the spectrum graph in Fig. 1. Fig. 1 shows that the graph produced almost same pattern and characteristics from different absorbance values. It can be seen that the higher the absorbance value, the higher the noise disturbance, and this condition was more affected by the equipment used. In a spectrum with a wavelength of less than 225 nm, the absorbance pattern was irregular due to the characteristics of solvent used, which having a cut-off limit of wavelength less than 225 nm, so the wavelengths below 225 nm were not analyzed in this study. Likewise for wavelengths 350-400 nm, it can be seen that there was no absorption of UV light, so in this wavelength range were not analyzed. So that the focus of the analysis was only in the range of 225-350 nm, where the spectrum pattern at those wavelengths can be seen in Fig. 2.

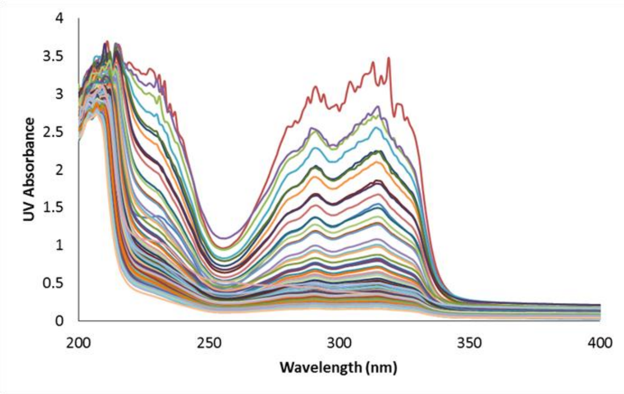

Fig. 1. *Absorption of the UV spectrum of Ciherang rice at various levels of DM*

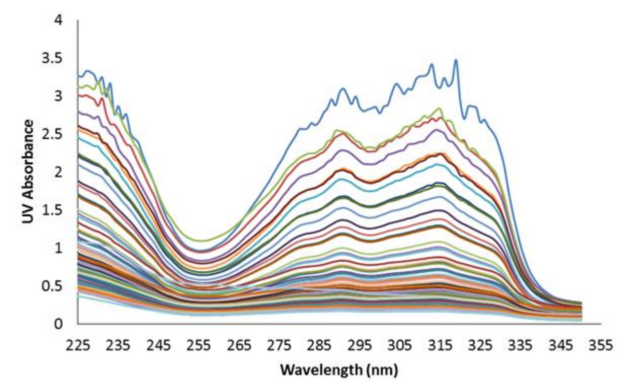

Fig. 2. *Absorption of UV rice spectrum at wavelengths of 225-350 nm*

Noise contained in the spectrum can be reduced through the smoothing process, in this case using the moving average method. Fig. 3 shows the results of the smoothing process that produced a new spectrum generated from the original spectrum, whitout changing the pattern and characteristics of the spectrum. Smoothing only smooths out irregular fluctuating values to facilitate further analysis.

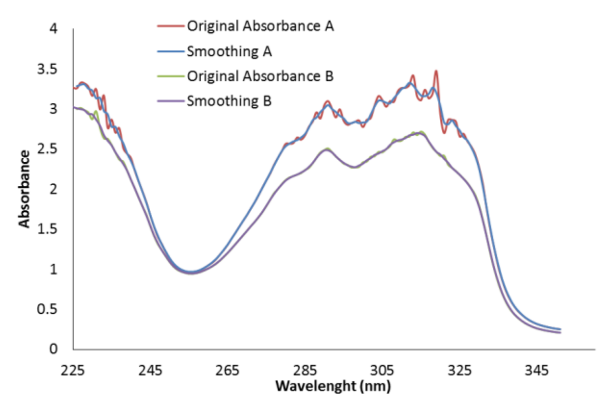

Fig. 3. *Absorbance of the UV spectrum at wavelength of 225-350 nm after smoothing.*

However, smoothing of the spectrum has not provided clearer information on the position of the most dominant wavelengths in absorbing UV light, so further data processing is needed in the form of derivatives to clarify the position of the dominant wavelength absorbing UV light. In Fig. 4, the first derivative process produced a spectrum pattern that showed the position of UV light absorbed more, but still in the wide wavelengths range as in the range of 330-335 nm, 290-300 nm and at 315-320 nm. Based on these conditions, the second derivative is done to locate the peak of the spectrum more clearly, because the second derivative value was relatively small, so it needs the normalization process of the virgin in the range of 0-1 to get a more visible graph. The normalized 2nd derivative shows a clearer wavelength peak which can be seen in Fig. 4.

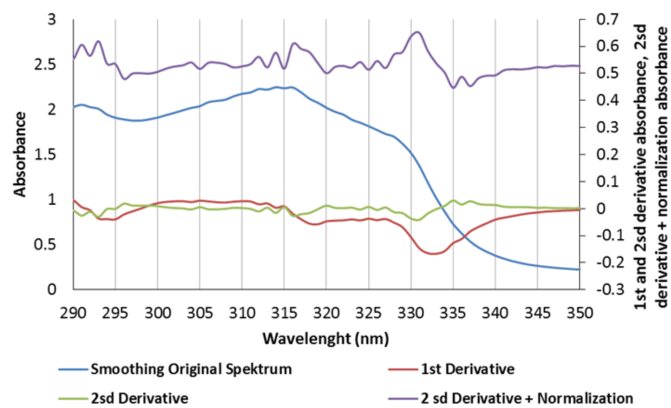

Fig. 4. *Spectral data at 290-350 nm wavelengths after several pre-treatment data*

The position of the peaks of absornace cotain information about characteristic of UV absorbance from rice solution. There are many elements on the surface of rice when rice is dissolved in n-hexan. Based on the type of solution used, the fat component is the component that is most expected to dissolve into the solution. Fat is the main component found on the surface of rice, so the longer the rice is polished, the fat component found on the surface of rice will decrease. Measure the remaining fat in the rice can be used as an indicator of DM value of rice [8]. In many studies, fat content was used as an indicator in determining rice DM such as the use of metylene blue, and then some visual measurements and color-based optical measurements were applied. The darker color of rice is used as a sign that more fat is still on the surface of the rice. Likewise, the whiter color of rice is used as a marker that less fat is found on the surface of rice. Fat content on the surface of rice will cause the shelf life of rice to be shorter, because the fat will quickly react with the air of the storage environment, and if this condition occurs it will make the rice become very dull in appearance and a rancid smell on rice appears. In addition, the color of white and clean rice is preferred by consumers so that the level of white rice is used as the main parameter in the classification of rice on the market which will determine the prices. In general, this level of whiteness is often correlated with rice DM, this is not entirely wrong but it is not appropriate in the definition of DM. DM is a reduced percentage of aleurone layer on the surface of rice as measured by the percentage of reduced weight of rice before milling with rice after milling. This definition was developed into a measurement method called the gravimetry. In the aleurone layer there are constituent elements, among others; fat, fiber, ash and other elements [4]. The mathematical model developed was an empirical model, where the model was generated from the measurement process and observations made on the sample used. The absorbance characteristics of the UV spectrum produced several peaks which are the characteristics of the rice solution, each peak carrying a certain information about the elements found on the surface of the rice. Determination of the spectrum peak that has the most strong relationship with DM rice was done by observing at the correlation between the peak of the spectrum and the DM value. In this study, the absorbtion peak was the highest correlation with DM is at a wavelength of 331 nm. The UV absorbtion peaks were produced by the process of electron translation found in its constituent elements, so the UV spectroscopic method is possible to produce a single wavelength to determine the influence of an element in its spectrum, in contrast to the NIR which is based on the bonding of its constituent molecules, so that an element is usually characterized by several wavelength peaks and wavelength range. Agricultural products have unique characteristics, one of the uniqueness is the interaction between the characteristics of the processing method. In general they have an exponential relationship, such as the decrease in water content of agricultural materials in the drying process and decay of vitamin C levels in food. The pattern of decreasing fat from the outer to inner surface layers of rice is exponential [4]. Based on this phenomenon, the model of the relationship between the absorbance characteristics at the UV spectrum and DM of rice was developed in the form of exponential equations, resulting in a relationship between DM and UV absorbance as shown in Fig. 5. Based on the characteristics [4], the relationship formed reflects the fat content dissolved into a rice solution.

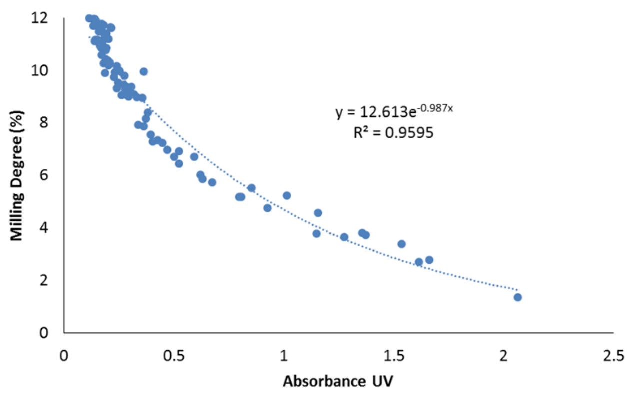

Fig. 5. *Model of DM by gravimetry relationship with UV absorbance characteristic values*

Based on the data of DM and UV absobance as shown in Fig. 5, the relationship can be expressed in a mathematical equation model as follows:

$$DM_{model} = 12.613\, e^{-0.987\, A_{\lambda_{331}}}$$

$A_{\lambda_{331}}$ = UV absorbance value at wavelenght 331 nm

This resulting model can be used to predict DM of rice based on the absorbance value of the rice solution. However, the model validation process is needed to observe the performance of the model that has been developed in predicting DM of rice based on UV absorbance value at a wavelength of 331 nm. The model validation results can be seen in Fig. 6.

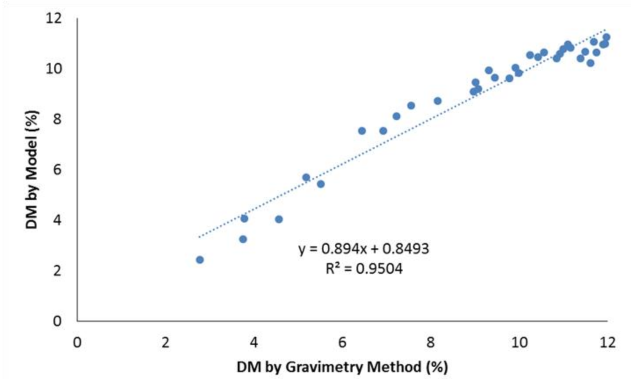

Fig. 6. *Model validation graph for DM value by gravimetry method*

Validation was carried out using 35 data sets from the original spectrum, the model validation results showed a good prediction DM value compare to measured DM value using the gravimetry method as the reference DM value. This was indicated by low estimated error value stated in the RMSEP value of 0.6193.

4 Conclusions

The absorbance value of rice solution at a wavelength of 331 nm in the UV spectrum can be used as data input in the development of an empirical mathematical model to predict DM of Ciherang variety of rice. The best mathematical model obtained in this study was an exponential equation with the coefficient of determination (R^2) of 0.9595. In addition, the mathematical model validation results in a coefficient of determination (R^2) of 0.9504 with RMSEP 0.6193.

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