Food and Applied Bioscience Journal, 2020, 8(2): 19-28

Effect of microwave and infrared vacuum drying on physicochemical properties of rice bran and their near infrared spectroscopy (NIR) prediction: partial least square (PLS) and principal component analysis (PCA)

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Abstract

Rice bran (RB) stabilized by drying methods at different power, time, and temperature conditions were subjected to be analyzed for chemical compositions and color changes. Compared to unstabilized RB (control), RB stabilized by microwave vacuum drying (at 700 and 800 W for 3 and 4 min) and infrared vacuum drying (at 65 and 70°C for 10 and 15 min) exhibited higher fat, carbohydrate, fiber, a* and b* values, but lower moisture, ash and L* value. Stabilized samples were measured by NIR to obtain spectrum. PCA was used exploratorily to analyze the NIR spectrum showing footprint of rice bran, which indicated a good separation of control and treated samples. The relationship between the NIR spectra and the physicochemical parameters was investigated using PLS. The high values of R^2 and Q^2 of the correlation graphs demonstrated that NIR was a good approach for observing the quality change of the processed RB.

Keywords: Microwave vacuum drying, infrared vacuum drying, near infrared spectroscopy, chemometrics, physicochemical properties

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Received: 26 February 2020, Accepted: 2 June 2020

1. Introduction

RB is rich in nutrients with 14-16% protein, 15-23% oil, 40-55% carbohydrate, and 7-19% fiber (Moongngarm *et al.,* 2012; Ramezanzadeh *et al.,* 2000). RB has the potential to be used as a food ingredient from the presence of its nutrients, for instance, substitution of wheat flour with the roasted riceberry rice bran in sandwich bread (Raungrusmee *et al*., 2019) and applying dietary fiber from rice bran into bread products to improve the quality and consumer acceptance (Singthong, 2016). Due to the presence of lipase in RB, it rapidly hydrolyzes oil to free fatty acid and glycerol, causing reduction in the RB quality. To reduce the problem, some stabilization techniques have been applied e.g. continue microwave oven (Pongrat and Songsermpong, 2019) and infrared vacuum drying (Thongluea et al., 2019). Even though stabilization techniques are able to protect RB from oxidation, they also affect the physicochemical property of RB (Loypimai *et al.,* 2015).

It is well known that NIR spectroscopy is based on the absorption of electromagnetic radiation between 750−2500 nm and it provides qualitative information on the composition of samples measured. Since absorption of NIR energy increases in overlapping overtones and combinations of rotation and vibration of different chemical bonds including C−H, O−H, and N−H, the chemical composition of the organic molecules can be determined using NIR (Williams, 2019). The application of NIR for determining parameters in RB such as protein, ash, crude oil, and moisture content were already employed in the previous study for fresh RB (Bagchi *et al.,* 2016). Moreover, it was applied to determine the gamma-oryzanol, which is a major bioactive compound found in rice bran oil (Pungseeklao *et al.,* 2016). Chemometric is the interpretation of data to deliver the information from those data. Partial least square regression (PLS) is one of the chemometric techniques that uses for finding the correlation between real data and prediction data (Diaz *et al.,* 2019). Principal component analysis (PCA) was previously employed as analyses of the data structure and as classification techniques (Fernández−Espinosa, 2016).

The objectives of the research were to study the effects of microwave and infrared heating on the physicochemical properties of RB and to apply the chemometrics to interpret the data of NIR and physicochemical properties by using PLS to find the correlation and PCA to cluster the group of data.

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2. Materials and Methods

2.1 Sample preparation

RB was obtained from a small local paddy factory (Banrai sub−district, Bangkratom district, Phitsanulok province, Thailand). RB was dried by microwave vacuum dryer (March cool industry Co. LTD, Bangkok, Thailand) under the conditions of 700 and 800 W for 3 and 4 min. Infrared vacuum dryer (March cool industry Co. LTD, Bangkok, Thailand) was operated under the conditions of 65 and 70°C for 10 and 15 min. The RB samples were kept in aluminum vacuum bag and stored in a freezer (-20°C).

2.2 Near infrared spectroscopy

In this experiment, the visible and near infrared reflectance spectra of RB samples were measured using FieldSpec 3 spectroradiometer from ASD Inc. (Boulder, Colorado) equipped with a Si array (350 to 1100 nm) and InGaAs (1100 to 2500 nm) detectors. Lowell pro-lamp with a correlated color temperature of 2901 K was used as the illumination light source. The light source and the read fiber were integrated within an ASD High Intensity Contact Probe. Before the reflectance measurement could be taken, the spectrometer was calibrated using a white diffuse reflectance standard.

RB samples composed of an unstabilized (control) and 8 stabilized treatments. The samples were put on the plate and measured at different positions (triplicates measurements per one sample). After that, all the samples were analyzed for physicochemical properties.

2.3. Physicochemical properties analyses

Moisture content (MC), proteins, fat, fiber, and ash contents were determined according to AOAC methods (AOAC, 2010). Carbohydrate was calculated from differences using the Equation 1:

$$\text{Carbohydrate} = 100-(\text{Moisture} + \text{Protein} + \text{Fat} + \text{Fiber} + \text{Ash}) \tag{1}$$

Color measurement was analyzed by Colorimeter (Coloflex EZ Spectrophotometer 45/0, USA) and reported as L* (lightness), a* (redness), and b* (yellowness) values. The total color differences (ΔE) between the control and treated samples were calculated using Equation 2: (Yeh *et al.,* 2002).

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \tag{2}$$

2.4. Statistical analysis

Duncan's multiple range tests were employed to determine the significance of differences among samples at $P<0.05$ level, using SPSS for Windows (version 17.0) program. All chemometric analyses, principal component analysis (PCA) and partial least squares (PLS), were performed using in-house MATLAB scripts (MATLAB V7.0, The Math Works Inc., Natick) (Wongsaipun *et al.,* 2018). The utilization of Standard Normal Variate was selected as it showed the most appropriate result for pre-data processing steps. The PLS model was optimized using leave-one-out cross-validation (LOOCV) method (Brereton, 2009). The predictive performance was presented using coefficients of determination (R^2 and Q^2) and root mean square error of calibration (RMSEC) and cross validation (RMSECV).

3. Results and Discussion

3.1 Effect of treatments on physicochemical properties of RB

The effect of microwave and infrared vacuum drying methods at different conditions on the physicochemical properties of RB are performed in Table 1. Moisture content (MC) plays an important role as the parameter of drying. MC ranged between 1.76-11.95% (dry basis; DB). The lowest MC was found in RB treated with microwave at 700 W for 4 min. The control sample contained the highest MC. It was noticed that samples treated by microwave contained lower MC compared to those treated by infrared drying. The range of protein content (PC) of both treated samples and control was between 14.15-17.87%. The lowest protein content was found in treated RB by microwave at 700 W for 3 min, whereas the highest PC was found in sample treated by microwave at 700 W for 4 min. It could be seen that factors affecting protein changes during drying were temperature and time. After treatment, changes of protein content were unpredictable compared to those of moisture content. This was assumed that temperatures and times applied in this study were not severe to cause changes in protein structures and contents. It was reported by other researchers that after stabilizing RB by increasing power density (2-6 W/g RB) and time (1-5 min) of microwave heating, protein varied with no certain trend between treated and non-treated RB (Patil *et al.,* 2016).

The fat and fiber content changes of RB after drying were observed in a similar trend. Samples treated with infrared and microwave showed a significant increase in fat and fiber contents, except the treated sample using microwave at 700 W for 3 min, which showed the lowest fat and fiber contents. The increase in fat and fiber content could be attributed to the fact that heat helped in breaking the molecular bonds especially the covalent bonds which tightly bound the fat and fiber to the cellular matrix (Terigar *et al.,* 2011). Carbohydrate content was significantly increased after RB samples were treated. This might be explained by treating

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samples with infrared or microwave could concentrate the remaining substances in bran, including carbohydrate component. The highest ash content was found in control sample as it was found that ash content was significantly decreased in the RB samples after drying treatments. This could be due to the loss of some minerals after treatment of microwave and infrared in this study. Laila *et al.,* (1994) also reported that the ash content of parboiled RB varieties decreased with microwave times of 3, 5, 6 and 8 min.

Color of RB depends on heating conditions such as power, temperature and time of each stabilization method. It was reported that all color values (L*, a* and b*) of RB were affected significantly ($P<0.05$) by infrared drying (temperatures of 100-140°C and times 5-20 min) (Irakli *et al.,* 2018). After stabilizing, L * was significantly decreased, while a* and b* values were significantly increased. The ∆E value indicated as a single value in color difference L*, a*, and b*, was also significantly different. Higher ∆E value indicated more color difference compared to control (unstabilized RB). It was found that stabilization of RB by both drying methods in this study caused color changes in RB. Patil *et al.* (2016) optimized the condition of microwave heating for stabilizing RB and reported that after using the best condition, moisture and fiber contents were decreased but ash, fat and protein were increased. However, some conditions did not affect the protein and fat contents. On the other hand, infrared heating changed the color of RB (Irakli *et al.,* 2018) and all treated RB samples exhibited significantly lower L* value, but higher a* and b* values in comparison with those of the control of unstabilized RB. In addition, Rodchuajeen *et al.* (2016) also reported that (∆E) of stabilized RB by infrared moving-bed drying methods (at 120, 160 and 180°C) were significantly different compared to control of unstabilized RB.

The NIR spectra of the RB samples were illustrated in Fig 1a where the spectrum line colors demonstrate different drying conditions. The spectra with green, blue and red lines were represented the samples of control, microwave and infrared treated methods, respectively. The feature characteristics of each spectra group could only be slightly observed. However, the difference was more perceivable after the data were processed using PCA as presented in Fig 1b. The score plot in Fig 1b revealed that Control and M 700/3 conditions were located on the upper space of the graph, while the others were clustered at the lower part. It implied that the drying with microwave at 700 W for 3 min did not considerably alter the RB sample. Meanwhile, varied heating conditions with microwave and infrared could result in the similar trends for the processed samples.

Table 1 Effect of microwave and infrared vacuum drying on physicochemical properties of RB

Stabilization		Content (%, dry basis)									
Method	**Condition**	Moisture	Protein	Fat	Fiber	Ash	Carbohydrate	L*	a*	b*	ΔE
	Control	11.95 ±0.04^{a}	16.30 ±0.70^{bc}	21.46 ±0.14^{c}	6.69 ±0.11^{c}	10.17 ±0.12^{a}	33.42 ±0.90^{e}	66.58 ±0.01^{a}	2.30 ±0.01^{f}	16.11 ±0.03^{f}	
Micro wave vacuum	700 W, 3 min	2.09 ±0.00^{f}	14.15 ±0.16^{d}	18.70 ±0.67^{d}	5.19 ±0.11^{d}	8.70 ±0.11^{b}	51.17 ±0.58^{a}	65.93 ±0.02^{b}	2.49 ±0.01^{e}	17.11 ±0.05^{c}	1.21 ±0.05^{g}
	700 W, 4 min	1.76 ±0.12^{g}	17.87 ±0.16^{a}	24.11 ±0.31^{ab}	8.65 ±0.16^{b}	8.47 ±0.45^{bc}	39.13 ±0.92^{bc}	61.50 ±0.00^{d}	3.14 ±0.03^{b}	17.01 ±0.03^{d}	5.23 ±0.01^{e}
	800 W, 3 min	1.99 ±0.04^{f}	16.22 ±0.86^{bc}	24.00 ±0.12^{ab}	9.75 ±1.22^{a}	8.22 ±0.05^{c}	39.82 ±0.55^{b}	61.63 ±0.02^{c}	3.04 ±0.02^{c}	16.92 ±0.01^{e}	5.08 ±0.02^{f}
	800 W, 4 min	2.00 ±0.12^{f}	16.08 ±1.06^{bc}	23.77 ±0.16^{b}	10.68 ±1.10^{a}	8.24 ±0.08^{c}	39.22 ±0.63^{bc}	60.48 ±0.01^{g}	3.21 ±0.03^{a}	16.93 ±0.02^{e}	6.23 ±0.01^{a}
Infra red vacuum	65 °C, 10 min	2.65 ±0.13^{e}	16.82 ±0.22^{ab}	24.25 ±0.14^{ab}	10.79 ±0.11^{a}	8.64 ±0.12^{b}	36.85 ±0.50^{d}	61.22 ±0.01^{f}	3.00 ±0.02^{d}	17.41 ±0.02^{b}	5.56 ±0.01^{bc}
	65 °C, 15 min	3.04 ±0.03^{d}	16.75 ±0.26^{ab}	24.59 ±0.26^{a}	10.27 ±0.88^{a}	8.53 ±0.07^{bc}	36.81 ±0.82^{d}	61.21 ±0.01^{f}	3.05 ±0.02^{c}	17.46 ±0.05^{b}	5.59 ±0.01^{b}
	70 °C, 10 min	3.84 ±0.12^{b}	15.08 ±0.54^{cd}	24.37 ±0.23^{ab}	9.87 ±0.13^{a}	8.52 ±0.04^{bc}	38.32 ±0.29^{c}	61.28 ±0.00^{e}	3.03 ±0.02^{cd}	17.50 ±0.01^{a}	5.53 ±0.00^{c}
	70 °C, 15 min	3.46 ±0.06^{c}	15.45 ±1.11^{c}	23.90 ±0.22^{b}	10.60 ±0.06^{a}	8.44 ±0.13^{bc}	38.15 ±1.39^{cd}	61.50 ±0.00^{d}	3.23 ±0.01^{a}	17.79 ±0.04^{a}	5.43 ±0.01^{d}

W: watts. Values are expressed as mean ± standard deviation (n=3). Different alphabet indicates significant difference in same column (P<0.05) by Duncan's Multiple Range Test (DMRT)

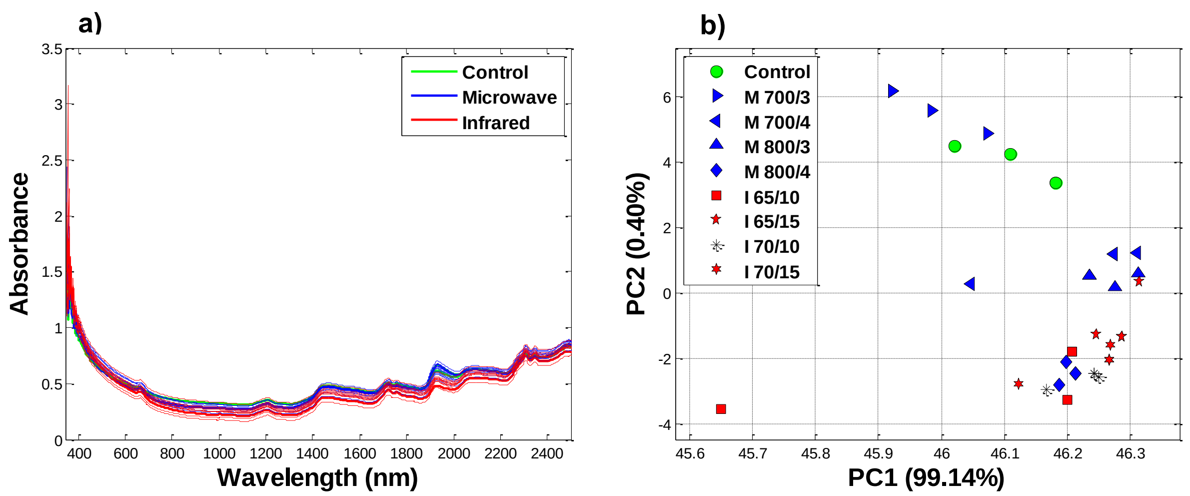

Fig 1 a) NIR spectra of RB samples at different drying conditions and b) PCA score plot of RB samples at different conditions by using Standard Normal Variate (SNV) as data preprocessing. PC1 is the axis explaining the most variability among the samples including in the study and PC2 is the largest amount of variation that has not been captured by PC1.

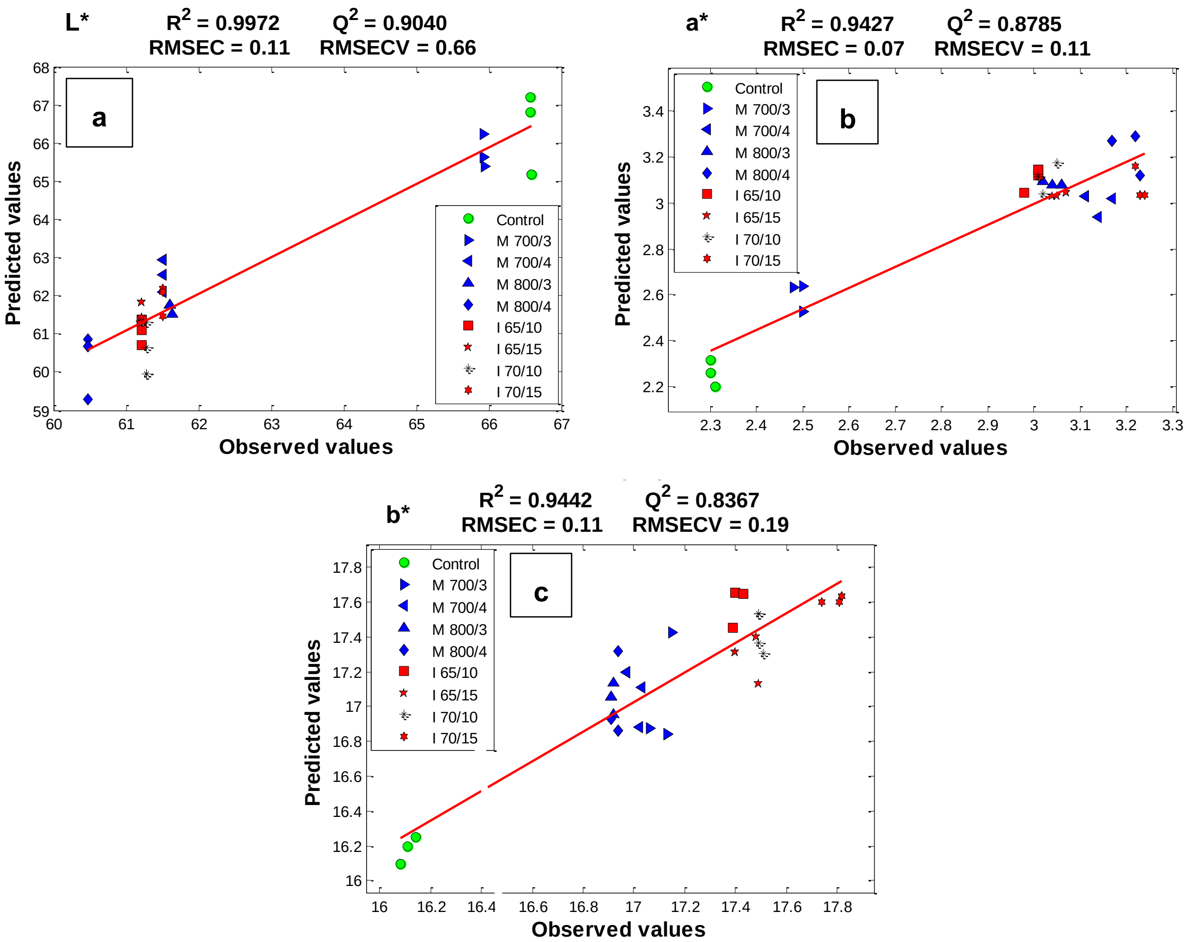

Fig 2 PLS prediction of data from NIR and color analysis (L*, a*, and b*) of RB samples at different drying conditions: a) L*, b) a* and c) b*

In relation to the color and physicochemical parameters, the PLS prediction based on the recorded NIR spectra was established. Based on the prediction mode of the LOOCV, the correlation graph demonstrating the observed and predicted values of the color and physicochemical parameters are presented in Fig 2 and Fig 3, respectively. The samples processed at different drying methods were shown in different marker colors (green = control, blue = microwave and red = infrared vacuum dryer). In all cases, the lower of Q^2 when compared to the R^2 together with the higher of the RMSECV when compared to the RMSEC demonstrated the eligibility of the PLS model for the calibration tasks and the models were not prone to over fitting. In Fig 2, the Q^2 values closed to 1 revealed a good relationship between NIR spectra and color changed of the RB. Considering the color changes, it was noticed that heating generated by microwave drying method played more important roles than in infrared drying in changing of L* and a* values as the moisture loss during heating could cause samples to be darker after treatment.

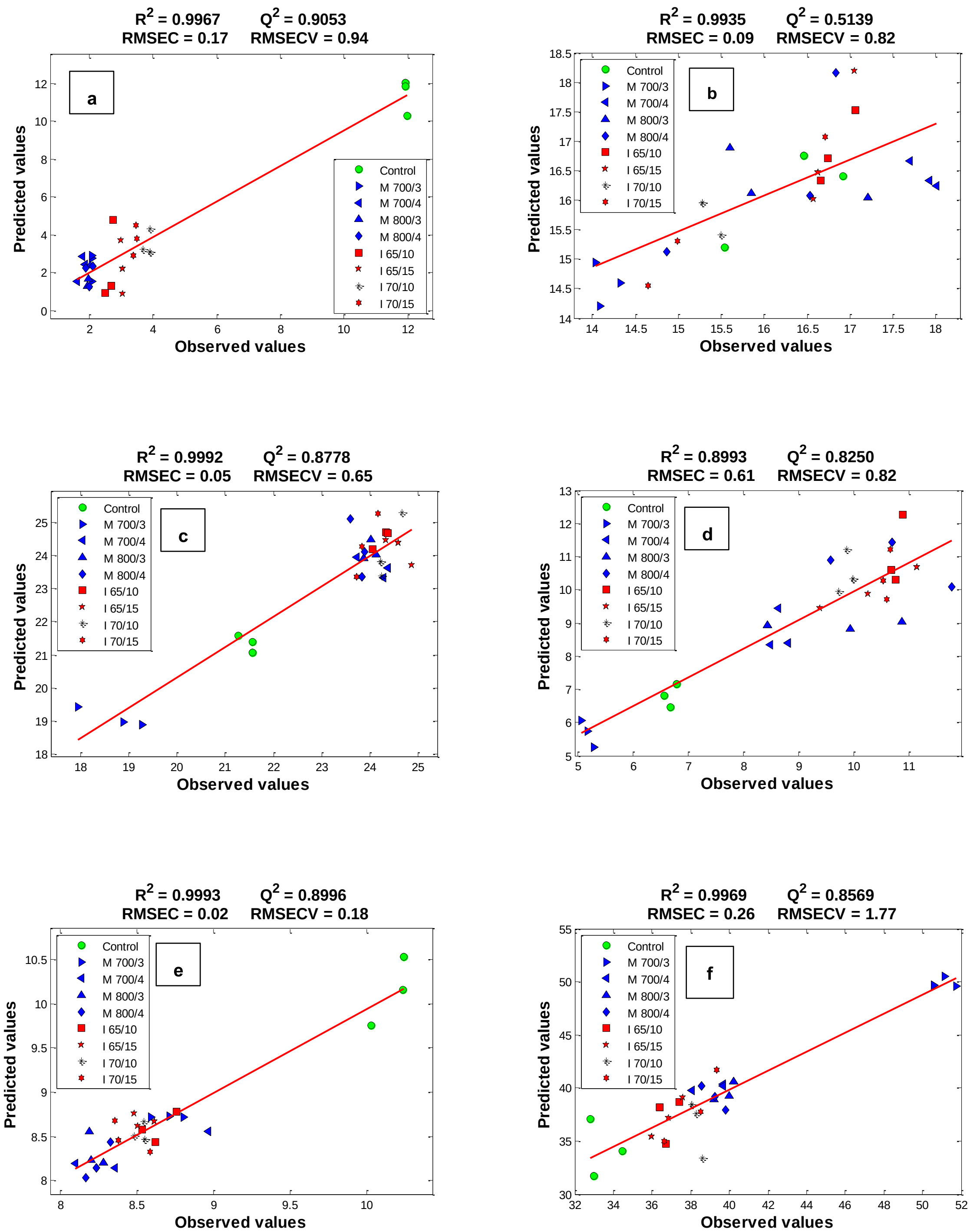

Fig 3 PLS prediction of NIR and chemical compositions of RB that are a) MC, b) protein content, c) fat, d) fiber, e) ash and f) total carbohydrate.

Fig 3a - Fig 3f represented the prediction of MC, protein, fat, fiber, ash and total carbohydrate contents, respectively. From those results, most chemical compositions provided satisfied predictive results, however, the protein content (Fig 3b) had the lowest Q2. The NIR data had good correlation with several chemical compositions in the RB samples except protein. Considering the changes of RB during drying, there was no noticeable change in

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protein content. Whereas, the decreased trends of MC (Fig 3a) and ash (Fig 3e) contents were observed during drying with microwave (power and time condition) and infrared vacuum dryer (temperature and time condition) compared with unstabilized RB. However, there were increasing trends in fat (Fig 3c), fiber (Fig 3d) and carbohydrate (Fig 3f) contents. Remarkably, from those three chemical compositions, fat and fiber contents in RB were dropped when the microwave heating at 700 W for 3 min was performed. On the other hand, this drying could cause the increase trend in total carbohydrate content.

4. Conclusion

Stabilization of RB by microwave and infrared drying significantly affected chemical compositions and colors of RB. The changing patterns of the processed RB could be observed using PCA and PLS. Based on the analysis results of PLS calibrations, fat, carbohydrate, fiber a* and b* values increased, while moisture, ash and color of L* value decreased after the treatment.

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