Study Of The Drying And Bioactive Compounds Degradation Kinetics Of Of Germinated Soybean Seeds During Microwave Processing

Duong Thi Phuong Lien
Food Technology Department, CanTho University
CTU
CanTho, Vietnam
dtplien@ctu.edu.vn

***Abstract*—In this study, the effects of microwave (MW) processing of germinated soybean seeds on moisture content and total polyphenol content (TPC) were studied. Germinated soybeans were processed at three different MW output powers (140, 280, and 420 W). By increasing the MW output powers (140–420 W), the drying time decreased from 15 to 6 min. The drying process took place in the falling rate period. Seven mathematical models for describing the thin-layer drying behavior of samples were investigated. The models were compared based on their R^2, RMSE and χ^2 values between experimental and predicted moisture ratios. The results show that the Midilli model is the most appropriate model for drying behavior of thin layer samples. In addition, the kinetic study for the TPC degradation was conducted. According to the results, first-order kinetic models were fitted to experimental data. The activation energies of drying and TPC degradation process were 6.58 and 7.17 (W/g), respectively.**

Keywords— germination; kinetic; microwave drying; phenolics; soybeans

I. INTRODUCTION (*Heading 1*)

The soybean (*Glycine max* L. *Merrill)* belongs to the family Leguminosae and have been extensively consumed worldwide due to their abundant nutrients and functional compounds such as polyphenols that were natural antioxidants being great significance from functional point of view [1]. However, the acceptance of consumers for soybeans were limited due to unpleasant bean flavour, bitter taste [2,3] and the presence of antinutritional factors such as trypsin inhibitors, oligosaccharides and phytic acid [4]. Germination processes have been developed to overcome some of the disadvantages associated with soybean seeds because of an increase in nutritive value such as high in protein, vitamins and bioactive compounds and reduced antinutrients [5].

Thermal processing is one of the common methods used in food technology. This process can change in sensory qualities as well as nutritional as functional compounds degradation [6]. So, thermal processing techniques aim to minimize these changes in food materials. Many conventional thermal methods such as air flow drying, vacuum drying, and freeze-drying were used in food technology. The main disadvantage of these techniques was requiring long drying times at relatively high temperatures causing undesirable thermal degradation of the finished products [7,8]. Electro heating, a group of novel thermal processing techniques, such as ohmic (OH), MW, and radio frequency (RF) heating, has been developed for processing better foods [6,9,10]. MW irradiation, heat is generated directly inside the product by the friction of solvent molecules upon themselves, so there is no external heat transfer resistance. For this reason, MW treatment reduces drying time and to improve food quality by the way of reducing the degradation of nutrients and antioxidants as polyphenols [11], For this reason, researching of drying and phenolics degradation kinetics that is one of the most important aspects of drying process is very important and necessary.

II. MATERIALS AND METHODS

A. *Soybean Seeds And Germination Process*

Soybeans (MTD 760 variety) were supplied from Department of Genetics and Plant Breeding, College of Agriculture and Applied Biology, CanTho University. Soybeans were cleaned and rinsed with clean water before being soaked for 12 hours at ambient temperature (30 ± 2^{o}C). The soaked beans were drained, rinsed and placed in a germination chamber in dark condition. Watering automatically the seeds was set up two minutes for every 4 hours with cleaned water. Germination of soybean seeds was processed at 25^{o}C for 36 hours. Germinated soybeans were washed and drained before drying [12].

B. *MW drying process*

MW processing was carried out using a programmable MW oven (BIACKER, 23 L). MW heating was performed at 140, 280, and 420 W. Germinated soybean seeds (30±0.1 g) were spread as a layer on the Petri-dish that were placed on a rotating plate in MW oven. The samples were dried until the moisture content was around 5% (w.b). The moisture loss of samples was measured by weighing on the digital balance at 0.5–1 min intervals during the drying process. All measurements were carried out in triplicate. The processed material was cooled to room temperature and kept in a plastic bag until the analysis. Moisture contents (M) and total phenolic contents (TPC) were then determined. The extraction procedure for analysis of the TPC followed the studied results of Duong et al*.* (2015) [13].

C. Analysis Of TPC

The TPC was estimated by Folin-Ciocalteu method [14]. The TPC of samples was expressed as milligrams garlic acid equivalents per gram of dry matter (mg GAE/g).

D. Mathematical Modelling

Modeling of drying process

In order to effectively study the drying kinetics of foodstuffs, the effective modeling of drying behavior is necessary. The moisture ratio (MR) from experimental drying of germinated soybean seeds at different MW powers were fitted with seven thin-layer drying mathematical expressions proposed by several authors as listed in Table 1.

TABLE I. MATHEMATICAL MODELS FOR THE DRYING CURVES

Model name	Model	Reference
Lewis	MR = exp (-kt)	[15]
Page	MR = exp (-kt^n)	[16]
Modified Page	MR = exp (-(kt)^n)	[17]
Henderson and Pabis	MR = a×exp (-kt)	[18]
Logarithmic	MR = a×exp (-kt) + b	[19]
Wang and Singh	MR = 1 + bt + at^2	[20]
Midilli et al.	MR = a×exp (-kt^n) + bt	[21]

The moisture ratio of samples during the drying experiments was calculated using equation (1) [22].

$$MR = \frac{M_t - M_e}{M_o - M_e} \quad (1)$$

Where: MR is moisture ratio (dimensionless); M_t is the moisture content an any time, M_e is equilibrium moisture content, and M_o is initial moisture content (% d.b.).

Modeling of TPC degradation

The experimental data was used for the kinetic modeling to determine the degradation kinetics of TPC of germinated soybean seeds during MW processing. Many authors [6,8,23,24] recommend that the degradation of most bioactive compounds follows first order kinetics (2).

$$C_t = C_o . \exp(-kt) \quad (2)$$

Where C_t is the parameter at predefined time t, C_o is the initial value of the parameter, k is the reaction rate constant at MW output power (W), and t is the MW processing time (min).

Drying rate

The drying rate (DR) was calculated by the following formula (3) [25]:

$$DR = \frac{M_t - M_{t+\Delta t}}{\Delta t} \quad (3)$$

Where: $M_{t+\Delta t}$: moisture content at t+Δt (kg water/kg, d.b); t: drying time (min).

Activation energy

The activation energy (E_a) is found as modified from the revised Arrhenius equation (4). It is assumed as related to the drying kinetic constant rate (k, min^{-1}) and the ratio of MW output power to sample weight (m/P) instead of to air temperature. Activation energy can be determined by the graphic representation between ln(k) versus m/P [26,27].

$$k = k_o \exp\left(\frac{-E_a \times m}{P}\right) \quad (4)$$

E. Statistical analysis

Statistical evaluation and non-linear regression analyses were carried out using CurveExpert Professional 2.4.0 software. The statistical parameters used to determine the model that describes in the best way the variation in the moisture ratio values was the coefficient of determination (R^2), reduced chi-square (χ^2), and root mean square error (RMSE). The higher the R^2 and lower the χ^2 and RMSE values, the better is the fitting procedure [6,25,27,28]. The χ^2 and RMSE were determined as equation (5) and (6). Among these criteria RSME and χ^2 values were calculated by Microsoft Excel 2010 program, while R^2 was determined by the CurveExpert Professional 2.4.0 software.

$$\chi^2 = \frac{\sum_{i=1}^{N}(MR_{exp,i} - MR_{pre,i})^2}{N-z} \quad (5)$$

$$RMSE = \left[\frac{1}{N}\sum_{i-1}^{N}(MR_{pre,i} - MR_{exp,i})^2\right]^{1/2} \quad (6)$$

Where: $MR_{exp,i}$, $MR_{pre,i}$– experimental and predicted dimensionless moisture ratios, respectively; N– number of observations; z– number of constants.

III. RESULTS AND DISCUSSION

A. Fitting of Drying Curves

The change in moisture ratio of samples with time by MW drying was displayed in Figure 1. The graph in Figure 1 showed clearly that the moisture ratio decreases continuously with drying time from the initial 63.9% (w.b) to a final moisture content of 4.96%, 4.33%, and 4.95% (w.b) at a drying time of 15, 10 and 6 minutes, respectively.

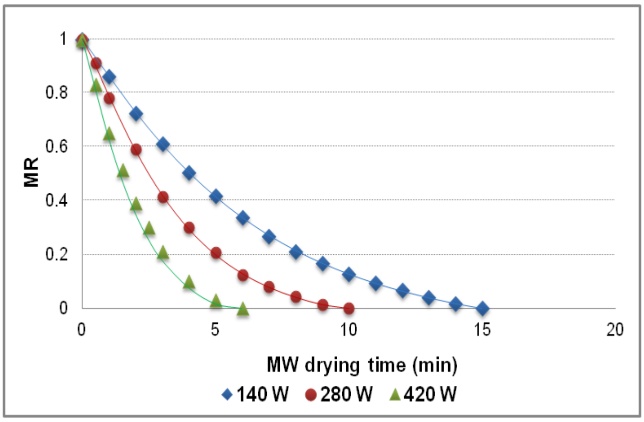

Fig. 1. *Change in MR during MW drying*

In addition, at the same drying time, the moisture ratio rapidly decreases as the MW power density increases. This phenomenon can be explained as following: the MW penetrated directly into the sample, so the heat was generated inside the sample and provided fast and uniform heating throughout the entire product, thus creating a large vapor pressure differential between the centre and the surface of product and allowing rapid transport and evaporation of water. This resulted in the significant decrease in drying time with the increase in MW output power. Similar results were found by many authors, such as the study on MW drying modeling of Brussels sprouts [6], of pepper [27], of Mabonde banana [29], of sugarcane bagasse [11].

The results of the statistical computations for the MW drying data given in Table 2 are considered to assess the fitting ability of drying models. It gives the values of the coefficients and statistical parameters for the seven respective models.

Among the all drying models, the middili et al model was selected as the most suitable model representing the thin layer MW drying of germinated soybean seeds, based on the criteria of the highest R^2 (0.9996–0.9999), the lowest χ^2 (0.00078–0.00001) and RMSE (0.0024–0.0042) with all applied values of to MW power (Table 2). It is also determined that the value of the drying coefficient (k) decreased with the increase in MW power. This signifies that with the increase in MW power density drying curve becomes steeper indicating faster drying of the product.

To validate the selected model, plots of experimental MR and predicted MR by Midilli et al. model were done and shown in Figure 2. The values of the coefficient determination (R^2) for the straight line obtained were 0.999, 0.999, and 0.998 corresponding to MW power of 140, 280, and 420 W. It means that the data points generally banded around a 45° straight line on the plots. This indicated for the suitability of the model to forecast the drying characteristics of germinated soybean seeds.

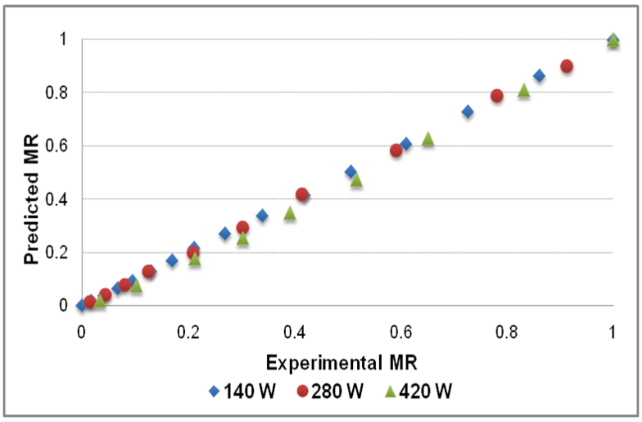

Fig. 2. *Relationship between experimental MR and predicted MR*

The result of Midilli et al. model selection was in agreement with previous studies, for example, studying on modeling MW drying kinetic of green bean slices [25], parsley [30], white mulberry [31], black pepper [32], banana … The Midilli et al. model has also been suggested by many authors to describe the other drying techniques, such as studying on modeling air convective drying kinetic of tomato [33], studying on modeling sun drying kinetic of green bean and okra [34], studying on oven, MW and sun drying of pomegranate fruit [35], studying on fluidized bed drying of olive pomace [36].

B. Drying Rate

The drying rates of germinated soybean seeds versus the drying time under different MW power were calculated using equation (3) and were displayed in Figure 3. The data on the graph showed that after an initial period of sample heating, the drying rate reached its maximum value, and then it decreases gradually with a decrease of moisture content in the samples. The moisture content of the material was very high during the initial phase of the drying which resulted in a higher absorption of MW power and higher drying rates due to the higher moisture diffusion. As the drying progressed, the loss of moisture in the product caused a decrease in the absorption of MW power and resulted in a fall in the drying rate. The absence of a constant drying rate period may be due to the thin layer of product that did not provide a constant supply of water in the specified period of time. Also, some resistance to water movement may exist due to shrinkage of the product on the surface, which reduces the drying rate considerably [37].

Similar findings were also reported by several authors for various foods under MW drying [11,27,37-39].

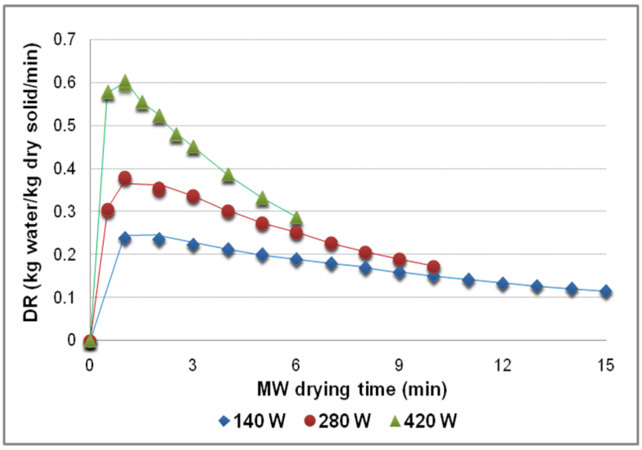

Fig. 3. *Change in drying rate during MW drying*

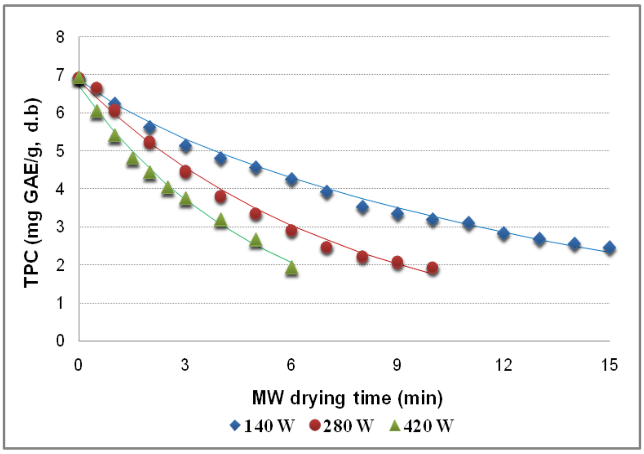

Fig. 4. *Change In TPC during MW drying*

C. TPC degradation kinetic

The changes in TPC of germinated soybean seeds during MW drying were presented in Figure 4. The TPC decreased as the MW drying time as well as MW power increased. The TPC was fitted to a first-order reaction kinetics model and the first-order rate constants (k) were given in Table 3. The MW power dependence of the rate constant was modeled by the Arrhenius-type relationship (4).

Erbay and Icier (2009) reported that a long term effect of temperature should cause a complete damage of the phenolic compounds, for this reason, both the degree of intense heat and heat treatment time were important [40].

TABLE II. DRYING CONSTANTS AND COEFFICIENTS OF DIFFERENT MODELS FOR ALL MICROWAVE POWER VALUES

Model R	P(W)	Constants and coefficients	R^2	χ^2	RMSE
1. Newton (Lewis)	140	k = 0.1889	0.9938	0.00124	0.0341
	280	k = 0.3097	0.9941	0.00111	0.0323
	420	k = 0.4863	0.9938	0.00086	0.0284
2. Henderson and Pabis	140	k = 0.1972, a = 1.046	0.9951	0.00105	0.0303
	280	k = 0.3256, a = 1.0498	0.9958	0.00084	0.0272
	420	k = 0.5076, a = 1.0409	0.9951	0.00074	0.0254
3. Logarithmic	140	k = 0.1478, a = 1.141, b = 0.129	0.9998	0.00004	0.0057
	280	k = 0.2556, a = 1.1298, b = -0.1043	0.9992	0.00017	0.0116
	420	k = 0.3952, a = 1.1386, b = -0.1217	0.9994	0.00010	0.0091
4. Modified Page	140	k = 0,1834, n = 1.2083	0.9989	0.10405	0.3017
	280	k = 0.3005, n = 1.2378	0.9993	0.05047	0.2101
	420	k = 0.4816, n = 1,2295	0.9992	0.02754	0.1552
5. Page	140	k = 0.1287, n = 1.2083	0.9989	0,00025	0,0146
	280	k = 0.2258, n = 1.2378	0.9993	0.00012	0.0104
	420	k = 0.4073, n = 1.2294	0.9992	0.00012	0.0103
6. Wang and Singh	140	a = 0.0049, b = -0.1380	0,9987	0.00028	0.0157
	280	a = 0.0125, b = -0.2224	0.9987	0.00026	0.0152
	420	a = 0.0333, b = -0.3632	0.9991	0.00014	0.0111
7. Midili	140	a = 0.9993, b = -0.0042, k = 0,1428, n = 1,093	0.9999	0.00001	0.0024
	280	a = 1.0028, b = -0.0038, k =0.2353, n = 1,1609	0.9998	0.00004	0.0056
	420	a = 0.9999, b = -0.0077, k = 0.4542, n = 1.1486	0.9999	0.00078	0.0042

TABLE III. THE FIRST-ORDER RATE CONSTANTS FOR TPC DEGRADATION

MW power (W)	k (min^{-1})	R^2
140	0.068	0.989
280	0.135	0.991
420	0.196	0.990

D. Activation energy

Activation energy of both drying and degradation processes can be calculated from the (K–m/P) curve and equation (4). E_a values of drying and TPC degradation processes were estimated respectively as 6.58 and 7.17 (W/g).

The activation energy of celery leaves was found in range of 6.92–7.89 W/g corresponding to the increase in MW output power from 180 to 900 W [41]. The reported values of 5.54 W/g mentioned for drying of okra [42]. The activation energy was found to be 7.72 W/g for 1.5 cm bed thickness of parboiled paddy with MW power from 180, to 720 W [39].

CONCLUSION

The seven thin layer models were used to describe the MW drying kinetics of the germinated soybean seeds. The Midilli model provided the best fit. By increasing the MW power level, the drying rate were increased. Therefore, drying time could be reduced. The first-order kinetic model was determined as the most appropriate model to represent the change of TPC of germinated soybean seeds during all MW processing. It is proved that the quality retention of green vegetables like germinated soybean seeds during MW processing was directly related to the intensity of MW power applied. The activation energy drying and TPC degradation of germinated soybean seeds were found to be 6.58 and 7.17 (W/g), respectively.

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