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Drying kinetics and thermal degradation of phenolic compounds and vitamin C in full fat germinated soy flours

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Abstract

The effects of temperature on drying kinetics, thermal degradation of phytonutrients and quality of full fat germinated soy flours were investigated. The drying process was conducted in the oven drier at the temperatures of 40, 50 and 60°C and the moisture contents of final products were lower than 5%. The first order equation was used for analysis drying kinetic and thermal degradation of total phenolic content (TPC), vitamin C and antioxidant activity expressed as DPPH radical scavenging percentage. Kinetic parameters k of each model showed high dependence on temperature and were evaluated by determination coefficient (R^2) that was calculated for goodness of fit. Arrhenius type equation was applied to determine the activation energy of moisture loss and degradation of vitamin C, TPC and antioxidant activity. These values were 53.14±1.77, 42.03±1.40, 33.44 ± 1.15 and 43.62±1.45 kJ/mol, respectively. Full fat germinated soy flour dried at 50ºC remained highest vitamin C, TPC, antioxidant activity as well as sensory quality.

Keywords: total phenolic content, vitamin C, free radical scavenging, IC50 value, kinetics

1. Introduction

Soybean is commonly consumed by people who are living in Southeast Asian countries due to their abundant nutrients and functional compounds, such as proteins, lipids, vitamins, fibers and phytochemicals [1]. However, the original content of some functional compounds in soybeans are low and they were not enough for functional benefits [2]. Germination processes have been developed in some countries 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 [3]. Now a day, soy flour is regarded as the most inexpensive vegetable protein of high quality which high protein content and all of essential amino acids needed for human beings [4]. Soy flour can enhanced protein content and quality of bread [5], cookies [6] and cakes without any negative effects on product quality [7]. Soy flour also used in processing frankfurters, bologna, meat loaves, meatballs, meat patties, and luncheon meats [8]. The main value of soy protein in meat products is to reduce formulation cost as well as the ability to improve viscosity, texture, firmness, moisture, overall yield, fat binding, emulsifying capacity, sensory properties and storage stability [9]. Germinated beans could also be used to replace, in part, wheat flour without affecting baking properties [10]. Full fat flour made from germinated soybeans is rich of nutrients and reduced antinutrients.

Drying is main technique in soy flour processing, however, it is well-known fact that harsh food processing steps have destructive effects on food components [11]. Food value compounds such as vitamin C, phenolic compounds are vulnerable to thermal processing [12]. Therefore, it is necessary to assay kinetic changes in bioactive components present in full fat germinated soy flour during drying process to determine optimum drying conditions with preserving phytonutrient contents of flours.

2. Materials and methods

2.1 Soybean and full fat germinated soy flours process

Soybeans (*Glycine max L.*, MTĐ 760 variety) were supplied from Department of Agricultural Genetic, College of Agricultural and Applied Biology, Cantho University.

Soybeans were cleaned and rinsed with cleaned water before being soaked for 12 hours to reach the equilibrium moisture content at ambient temperature (30 ± 2ºC). 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 25ºC for 36 hours. Germinated soybeans were washed and boiled for 10 minutes before drying [13]. Drying process was set up at 40, 50 and 60ºC until the moisture contents of samples reached 5±0.5%, and then the samples were ground to fine flour products.

After time intervals of drying process, samples were collected and freezed 1 day for freeze drying until moisture contents of samples lower than 5%. Moisture contents (MC), total phenolic contents (TPC), vitamin C and antioxidant activity assessed by DPPH radical scavenging percents were then determined. The extraction procedure for analysis of the antioxidant compounds followed the studied results of Duong *et al.* (2015) [14].

2.2 Determination of the TPC, vitamin C, antioxidant capacity and sensory quality

The TPC was estimated by Folin-Ciocalteu method [15]. The TPC of samples was expressed as milligrams garlic acid equivalents per gram of dry matter (mg GAE/g).

Ascorbic acid (vitamin C) content was determined by redox titration with iodine [16].

Antioxidant activity of the phytochemicals extracted from soybean was assessed by measuring their radical scavenging activity that was measured by the bleaching of the purple-

coloured methanol solution of 2,2-diphenyl-1-picrylhydrazyl (DPPH). This spectrophotometric assay uses stable DPPH radical as a reagent. The DPPH radical scavenging activity was evaluated from the difference in peak area decrease of the DPPH radical detected at 517nm between a blank and a sample [17]. Percentage of radical scavenging activity was plotted against the corresponding concentration of the extract (μg/ml) to obtain IC50 value in mg/ml. IC50 is defined as the amount of antioxidant material required to scavenge 50% of free radical in the assay system.
Scoring method was for sensory quality evaluation of final products. Colors, flavors and tastes of products were scored by 8 panellists with the scale as following: 5 – Excellent; 4 – very good; 3 – good; 2 – fair and 1 – poor.

2.3 Drying kinetics and thermal degradation kinetics of TPC, vitamin C and antioxidant activity

Drying kinetic was modeled by empirical equation of Newton [18] that used a relationship termed moisture ratio (MR) as a dependant variable (Equation 1). The MR related to the gradient of the sample moisture in real time (M_t) with initial moisture (M_o) and equilibrium moisture (M_e) [19]. The Newton empirical equation was expressed as equation 2.

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

$$MR = \exp(-kt) \quad (2)$$

Where k is kinetic parameters ($hour^{-1}$) and t is drying time (hours). In this research, the shrinkage and external resistance were assumed as negligible.
Thermally induced degradation of most bioactive compounds follows first order kinetics (Equation 3).

$$C = C_o.\exp(-kt) \quad (3)$$

Where C and C_o are the TPC, vitamin C contents and antioxidant activities after drying time t and at t = 0 hour, spectively, and the k is the kinetic constant ($hour^{-1}$).
In order to observe the influence of drying temperature on the kinetic parameters k, an Arrhenius type equation was applied (Equation 4), from which the activation energy (Ea, kJ/mol) is obtained, which shows sensitivity of the parameter to temperature [20]. Activation energy can be determined by the graphic representation between ln(k) versus T^{-1} (K).

$$k = k_o.\exp(-E_a/\text{RT}) \quad (4)$$

2.4 Statistical analysis

From the modeling data values, Regression analysis was used to determine the correlation coefficient (R^2) using Microsoft Excel 2007.

3. Results & Discussion

3.1 Drying kinetics of full fat germinated soy flous

Fig. 1 showed the variation of dimensionless moisture contents (MR) as a function of drying time at the three experimental temperatures. All the drying curves showed a clear exponential tendency and an increase in the temperature accelerated the drying process, which is very common in food materials drying processes [21, 22]. This is a typical case where moisture from the solid material evaporates first from the moisture layer on the surface and continuously decreases until water moves from the inside of the solid material by diffusion processes [23]. These results are comparable to those reported in previous studies for drying fruits and vegetables such as red papers [23], golden berry [24], strawberries [25] and sweet pepino [26]. In the present study, there was significant difference in the moisture content with different drying temperatures (p<0.05). At 40°C the drying rate was minimal and approached equilibrium after 18 h whereas equilibrium at 60C was attained after 7 h, representing 61.1% reduction in the total drying time.
The drying kinetics data obtained for the three applied temperatures was fitted to Newton empirical kinetic models due to the R^2 values ranged from 0.981 to 0.988 for the different temperatures (Table 1). The kinetic constants "k" were determined and Figure 1 also showed the predicted points obtained following the equation (2) for the three applied temperatures. Basing on drying curve the time required to reach desired moisture content can be estimated.

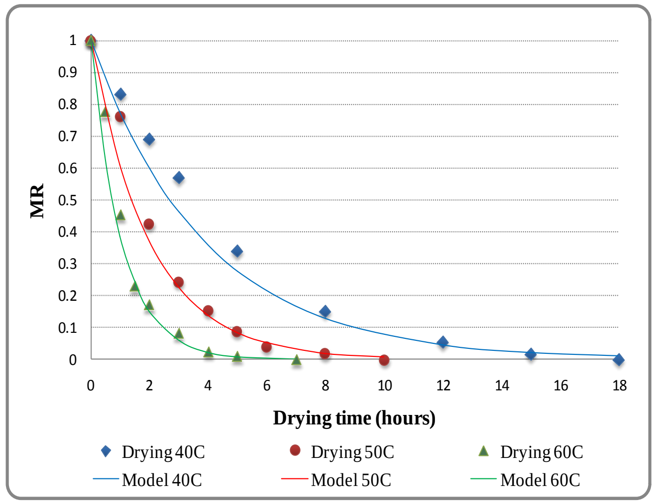

Fig 1: Experimental and calculated drying curves at the different working temperatures

Table 1: The kinetic constants and activation energy from drying process of full fat germinated soy flours

Temperatures (°C)	k	R^2	E_a, KJ/mol
40	$0.257^a \pm 0.02$	0.981	53.14±1.77
50	$0.497^b \pm 0.02$	0.988	
60	$0.949^c \pm 0.03$	0.984	

(Mean ± SD, The values showing different superscripts within a row are significantly different at p = 0.05)

In order to prove the dependence of kinetic constant 'k' on the drying temperature, the Arrhenius equation was applied, graphically representing ln(k) versus 1/T [20], from whose slopes activation energy (E_a, kJ/mol) were obtained. The kinetic constant 'k' and activation energy were presented in Table 1. Several authors have presented activation energy values, including Vega-Gálvez *et al.* (2009) [22] reported the activation energy of 51.05 kJ/mol for drying blueberry with the temperature from 60 to 80°C; Gupta *et al.* (2011) [27] reported the activation energy of 46.7 kJ/mol for drying brown seaweed with the temperature from 25 to 40°C. Senadeera *et al.* (2003) [28] reported the activation energy of 45.13 kJ/mol for fluidized bed drying of pea.

3.2 Thermal degradation of vitamin C, phenolic compounds and antioxidant activity of full fat germinated soy flous

Figures 2, 3 and 4 showed the dimensionless concentration ratio

(C/C_o) of vitamin C, phenolic compounds and antioxidant activity versus time. C is the concentrations at time (t) and C_o is concentratitons at t = 0. From the Figure 2, 3 and 4, the drying process showed a first order degradation for vitamin C, TPC and antioxidant activity. Some authors have shown that ascorbic acid, phenolic compounds and antioxidant activity degradation, in general, follows first order reaction kinetic [29, 30, 12]. The rate constant k is determined as the slope of Newton empirical kinetic models and it depended on inverse absolute temperature and activation energy by an Arrhenius type relationship. These parameters of the degradation of vitarmin C, phenolic compounds and antioxidant activity were displayed in Table 2.

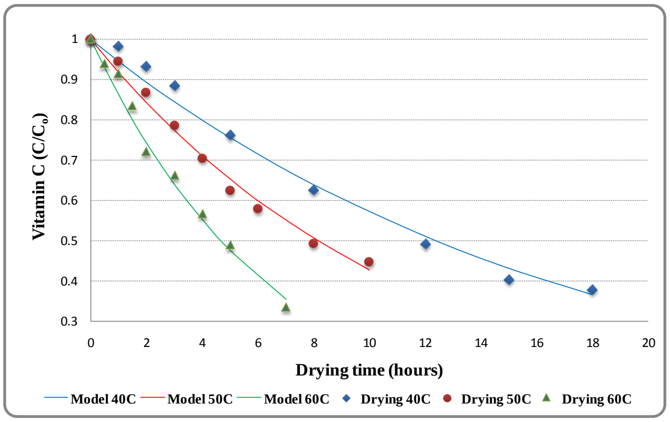

Fig 2: Experimental data and empirical kinetic models of vitamin C degradation

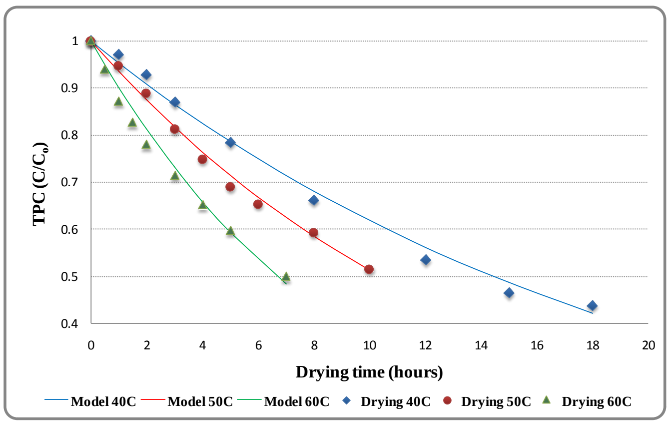

Fig 3: Experimental data and empirical kinetic models of TPC degradation

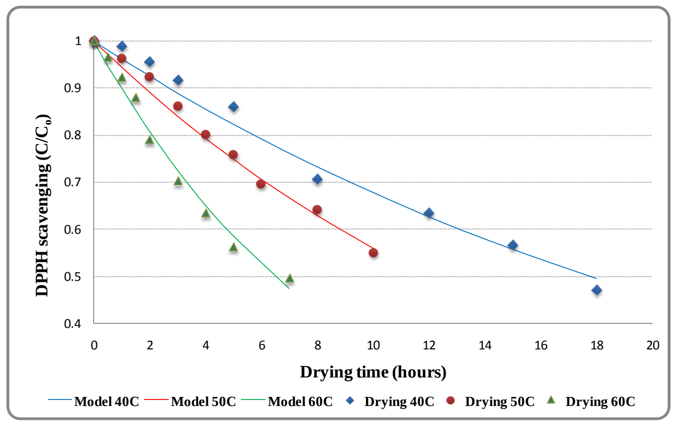

Fig 4: Experimental data and empirical kinetic models of antioxidant activity degradation

Table 2: The kinetic constants and activation energies from thermal degradation of vitamin C, TPC and antioxidant activity of full fat germinated soy flours

	Temperatures (°C)	k	R^2	E_a, KJ/mol
Vitamin C	40	$0.056^a \pm 0.008$	0.988	42.03±1.40
	50	$0.085^b \pm 0.007$	0.986	
	60	$0.148^c \pm 0.010$	0.987	
TPC	40	$0.048^a \pm 0.006$	0.989	33.44±1.15
	50	$0.067^b \pm 0.009$	0.991	
	60	$0.104^c \pm 0.011$	0.983	
DPPH scavenging	40	$0.039^a \pm 0.004$	0.984	43.62±1.45
	50	$0.058^b \pm 0.007$	0.984	
	60	$0.107^c \pm 0.009$	0.983	

(Mean ± SD, The values showing different superscripts within a row are significantly different at $p = 0.05$)

Due to the importance of vitamin C for human nutrition, it have been used as a quality indicator for food processes. The vitamin C can be easily degraded, depending on many variables such as pH, temperature, light, and presence of enzymes, oxygen, and metallic catalyzers [31]. Within them, temperature is one of the most important factors. It has been suggested that during drying process, the degradation of ascorbic acid can be described by first order kinetics [32, 33]. Orikasa *et al.* (2008) [33] applied a first order rate equation to the changes in ascorbic acid contents during hot air drying (40–70ºC) and found that the activation energy of 38.6 kJ/mol for the decomposition during drying of kiwi fruit. Regina (2007) [34] reported the ascorbic acid degradation activation energy of 77.96±7.01 kJ/mol from first order rate kinetic for drying (60–90ºC) of rosehip fruits.

The Figure 3 clearly showed that TPC decreased as a first order function of time and the degradation accelerated in parallel to an increase in temperature. Similar results were also determined by the authors studied on phytochemicals degradation kinetics for various food materials [35, 12, 36]. The TPC degradation are closely related to the temperatures applied at the drying process [12] and the Arrhenius model was used for describing thermal degradation kinetics of bioactive compounds. The results from Table 2 showed that higher E_a value associated with increased temperature dependence of TPC degradation and also implied that a smaller temperature elevation causes degradation of phytonutrients more rapidly.

The degradation of phenolic compounds is primarily caused by oxidation, cleavage of covalent bonds or enhanced oxidation reactions due to thermal processing [36]. Phenolic compounds degradation is accelerated with increasing temperature, which supports the data of degradation rate constant k shown in Table 2. The degradation of antioxidant compounds such as phenolics, vitamin C, vitamin E, β–carotene, etc led to decrease antioxidant activity. Thus, the antioxidant activity degraded during drying process and followed the first order reaction kinetic (Figure 4). The activation energy of antioxidant activity degradation was determined as 43.62±1.45 kJ/mol. Urrea *et al*. (2011) [37] found that the activation energy of antioxidant activity degradation of carrots during drying process (50–80ºC) was 23.7 kJ/mol.

3.3 Quality of full fat germinated soy flours

The full fat germinated soy flours were determined the quality index, such as contents of TPC, vitamin C, IC50 value and sensory quality. The results were shown in Table 3.

Table 3: Antioxidant characteristics and sensory quality of products dried at different temperatures

Drying temperatures (ºC)	40	50	60
Drying time (hrs)	18	10	7
TPC (mg GAE/g)	2.30^c±0.05	2.71^a±0.01	2.62^b±0.02
Vitamin C (mg/g)	2.28^b±0.04	2.71^a±0.03	2.03^c±0.03
IC50 (mg/ml)	16.81^a±0.22	15.59^c±0.56	16.42^b±0.15
Sensory quality			
Colors	4.3^a±0.3	4.5^a±0.4	3.6^b±0.3
Flavors	3.4^b±0.4	4.2^a±0.5	3.6^b±0.4
Tastes	3.1^b±0.2	4.5^a±0.6	3.5^b±0.5

(Mean, in db±SD, The values showing different superscripts within a row are significantly different at p = 0.05)

The flours dried at 50ºC remained highest TPC, vitamin C and antioxidant activity. In addition, the sensory quality scores for colors, flavors and tastes of this products were significant different to that of other products. For this reason, the drying temperature of 50ºC can be evaluated as the best collection for drying full fat germinated soy flours.

4. Conclusions

Phenolic compounds, with the antioxidant property, are considered food value components, and many studies have reported their bioactivity in human body. Therefore, it is important to develop or apply processing conditions not to extensively damage antioxidants present in foods. Germination of soybean seeds before processing is one of the effective methods in improving antioxidant properties of soybean seeds. Results obtained in this study showed that drying of full fat germinated soy flours at 50ºC preserves TPC, vitamin C as well as antioxidant activity in the final product compared with other products dried at 40 and 60ºC. This is a good evidence of the importance of examining drying kinetic and thermal degradation kinetic together. This study well reflected the drying kinetic and thermal degradation kinetic together for full fat germinated soy flours.

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