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Effect of air temperature on drying kinetics and quality characteristics of osmo-treated jumbo squid (*Dosidicus gigas*)

Antonio Vega-Gálvez [a], Margarita Miranda [a], Rodrigo Clavería [a], Issis Quispe [a], Judith Vergara [a], Elsa Uribe [a], Hector Paez [a], Karina Di Scala [b,c,*]

[a] Department of Food Engineering, Universidad de La Serena, Av. Raúl Bitran s/n, 599. La Serena, Chile
[b] Food Engineering Research Group, Universidad Nacional de Mar del Plata, Facultad de Ingeniería, Av. Juan B. Justo 4302. 7600 Mar del Plata, Argentina
[c] CONICET (Consejo Nacional de Investigaciones Científicas y Técnicas) Buenos Aires, Argentina

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ABSTRACT

The present study investigated the influence of air temperature on the drying kinetics, color, rehydration, total volatile basic nitrogen (TVBN), antioxidant capacity and texture of osmosed jumbo squid fillets during convective dehydration at 50, 60, 70, 80 and 90 °C. The Logarithmic and Two-term models could be used to describe the squid experimental drying curves. Discoloration of product was more noticeable at high drying temperatures where combined effects of non-enzymatic browning as well as protein denaturation modified the original color of the squid samples. Rehydration indexes showed a decrease while texture presented an increase with increasing air-drying temperature probably due to changes in food protein matrix. Total volatile basic nitrogen increased with process temperature. Antioxidant activity presented a decrease with temperature, especially at high drying temperatures. Results of this study demonstrated that the drying kinetics together with the reported quality attributes of the dried squid can be used to improve the final characteristics of the product.

1. Introduction

The jumbo or giant squid (*Dosidicus gigas*) is an important cephalopod and the major invertebrate of the pelagic seacoast of Chilean waters (Fernández & Vásquez, 1995; Rocha & Vega, 2003). The increasing demand for giant squid meat has enhanced the economic importance of this fishery industry in the last years due to its high-protein content and nutritional value (Abugoch, Guarda, Pérez, & Paredes, 1999). Fresh seafood is extremely perishable and the time to spoilage depends mainly on fish species, handling, processing and storage temperature (Tsironi, Salapa, & Taoukis, 2009). Usually, jumbo squid is sold as frozen or cooked frozen gutted mantle, but these procedures affect the quality attributes of the product (Valencia-Pérez et al., 2008; Yoshioka et al., 2003). Since quality of seafood is a driving force in the fish industry, it is necessary to develop new alternatives of processing in order to minimize the physical, chemical and biological reactions that lead to spoilage of this freshly caught seafood (Doe, 2000; Valencia-Pérez et al., 2008).

Drying is a traditional process that has been used for many centuries to preserve food and seafood (Barakat Mahmoud et al., 2006; Jain & Pathare, 2007; Vega-Gálvez, Andres, et al., 2009). The major objective of dehydration is the reduction of the food moisture content to a level at which microbial spoilage and deterioration reactions are minimized, which allows safe storage over an extended period of time (Doymaz, 2008; Vega-Gálvez, Di Scala, et al, 2009). In addition, it brings about substantial reduction in weight and volume, minimizing packaging, storage and transportation costs (Vega-Gálvez, Di Scala, et al, 2009). Traditionally, fish products are immersed in concentrated solutions to impregnate them with salt and/or other curing ingredients to prolong shelf life (Valencia-Pérez et al., 2008). Several authors have reported the osmotic process as a pre-treatment before drying in order to yield good quality products (Kehinde, Eshtiaghi, Ade-Omowaye, & Knorr, 2003). Generally, less drying time is also obtained with this pre-treatment (Fito & Chiralt, 2003; Rastogi, Raghavarao, Niranjan, & Knorr, 2002). Osmotic pre-treatment together with hot air convective drying present a promising combination of hurdle technologies leading to more stable fish products (Fito & Chiralt, 2003).

From a point of view of food product development, it is clear that the operations affect not only drying kinetics but also especially the final product quality (Di Scala & Crapiste, 2008; Fito & Chiralt, 2003; Vega-Gálvez, Di Scala, et al, 2009). Therefore,

* Corresponding author. Food Engineering Research Group, Universidad Nacional de Mar del Plata, Facultad de Ingeniería, Av. Juan B. Justo 4302, 7600 Mar del Plata, Argentina. Tel.: +54 223 4816600; fax: +54 223 4810046.
E-mail address: kdiscala@fi.mdp.edu.ar (K. Di Scala).

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optimization of the dehydration process is a challenging problem that demands the evaluation of many interconnected and opposing non-linear phenomena because food drying represents a complex process involving simultaneous mass and heat transfer in a hygroscopic system with variable properties and shrinkage (Di Scala & Crapiste, 2008). The knowledge of the drying kinetics contributes not only in the assessment of the intrinsic kinetics of the process but also to analyze the effect of the most relevant process variables on the performance of the operation itself from different points of view (process efficiency, energy yield, quality and safety of the products, etc.).

Mathematical models such as Newton, Henderson and Pabis, Page, Modified Page, Weibull, Two-term and Logarithmic have been applied to describe the drying characteristics of food materials (Doymaz, 2008; Jain & Pathare, 2007; Ait Mohamed et al., 2008; Vega-Gálvez, Andres, et al., 2009). However, in literature, the suitability of these models to the convective drying and the effect of air-drying temperature on the most important quality indexes of jumbo squid are scarce.

The aim of this research was to determine the influence of air temperature on the drying kinetics of osmosed jumbo squid fillets during convective dehydration at 50, 60, 70, 80 and 90 °C by simulating the experimental drying data with the mathematical expressions mentioned. In addition, the effect of the process variables on color, rehydration, total volatile basic nitrogen, antioxidant capacity and texture of the dried-rehydrated product were also evaluated.

2. Materials and methods

2.1. Raw material and osmotic pre-treatment

Jumbo squid (*D. gigas*) was obtained from a local fish market in Coquimbo, Chile. The main constituents of fresh squid were moisture 83.66 ± 0.23 g/100 g product, crude protein 18.88 ± 1.51 g/100 g product, lipid content of 1.88 ± 0.03 g/100 g product, ash 1.07 ± 0.02 g/100 g product and salt content of 1.12 ± 0.07 g/100 g product (Uribe et al., in press). The squids were maintained refrigerated at 4 °C for a maximum time of 12 h, prior to processing.

For this process, jumbo squid fillets were selected, and the external and stomach skin areas were discarded. Finally, the chosen selection was cut in cubes of 5.0 ± 0.1 cm each side, and 1.0 ± 0.1 cm thickness. The samples were immersed in salt solutions (NaCl, 6 g/100 mL) at a temperature of 85 °C (Uribe et al., in press). The brine to sample ratio was maintained at 8:1 in order to not dilute the osmotic solution by water removal during experiments. The brine was agitated continuously in a water bath (Quimis, Q.215.2, Sao Paulo, Brazil) to maintain a uniform temperature. The samples were kept in the osmotic solution for 20 min. After removal from the solution, the osmosed samples were rapidly blotted with absorbent paper to remove surface excess solution, and then weighed.

2.2. Drying experiments

The drying process was carried out in a convective tray dryer designed and built by the Department of Food Engineering of Universidad de La Serena (Vega-Gálvez, Di Scala, et al., 2009). The drying temperatures were 50, 60, 70, 80 and 90 °C. Air velocity was maintained at a constant rate of 2.1 ± 0.2 m/s in each test. It was measured with an omnidirectional anemometer (Extech Instrument Inc., 451112, Waltham, MA, USA). In addition, outlet relative humidity measured with an ambient digital hygrothermometer (Extech Instrument Inc., 451112, Waltham, MA, USA) was approximately 57.0 ± 3.8%. Samples (100.0 ± 1.0 g) of jumbo squid were used and arranged as a thin layer in a stainless steel basket, which hangs on a balance (Ohaus, SP402 Scout-Pro, Pine Book, NJ, USA) with an accuracy of ±0.01 g, communicated with an interface system (Ohaus, SP232 Scout-Pro, Pine Book, NJ, USA) connected to a personal computer, which records and stores the weight changes at time intervals defined by means of the Microsoft® Hyperterminal® software (Redmond, WA, USA). The experiments were finished at the point of reaching constant weight (equilibrium condition). The dehydrated samples were packed into polyethylene bags. Each experiment was done in triplicate.

2.3. Determination of the effective moisture diffusivity

Most food drying processes take place in the falling rate period, during which water is transported mainly by moisture diffusion (Doymaz, 2008; Vega-Gálvez, Andres, et al., 2009). The mathematical solution of Fick's second diffusion law, used to describe this period, when internal mass transfer is the controlling mechanism and one-dimensional transport in an infinite slab was assumed (Crank, 1975), Eq. (1). Moreover, for sufficiently long drying times, the first term in the series expansion gives a good estimate of the solution (Di Scala & Crapiste, 2008), Eq. (2). The dependent variable of this model, the moisture ratio (MR), was calculated using the mathematical expression of Eq. (3), which relates the gradient of the sample moisture content in real time (X_{wt}) to both initial (X_{wo}) and equilibrium moisture content (X_{we}).

$$MR = \frac{8}{\pi^2}\sum_{i=0}^{\infty}\frac{1}{(2i+1)^2}\exp\left[\frac{-(2i+1)^2 D_{eff}\ \pi^2 t}{4L^2}\right] \quad (1)$$

$$MR = \frac{8}{\pi^2}\exp\left[\frac{-D_{eff}\pi^2 t}{4L^2}\right] \quad (2)$$

$$MR = \frac{X_{wt} - X_{we}}{X_{wo} - X_{we}} \quad (3)$$

Where MR is the moisture ratio and D_{eff} is the effective moisture diffusivity (m^2/s), t is the drying time (s) and L is the half-thickness of the slab (m).

In practice, the effective moisture diffusivity for each temperature was calculated by plotting experimental drying data in terms of ln (MR) versus drying time and the D_{eff} value obtained from the straight line's slope (Di Scala & Crapiste, 2008; Doymaz, 2008). Moreover, the temperature dependence of the effective diffusivity can be represented by an Arrhenius relationship (Eq. (4)). Both kinetic parameters (E_a and D_o) can be estimated from the slope and intercept of the plot ln D_{eff} versus the reciprocal of absolute temperature (Di Scala & Crapiste, 2008):

$$D_{eff} = D_o\exp\left(-\frac{E_a}{RT}\right) \quad (4)$$

Where R is the universal gas constant (8.314 J/mol K), E_a is the activation energy (kJ/mol), D_0 the Arrhenius factor (m^2/s) and T is the absolute temperature (K).

2.4. Mathematical modeling of the drying curves

Experimental drying curves were fitted to seven thin layer-drying models, namely, Newton (Vega-Gálvez, Andres, et al., 2009), Henderson–Pabis (Vega-Gálvez, Andres, et al., 2009), Page (Jain & Pathare, 2007), Modified Page (Jain & Pathare, 2007), Weibull (Corzo, Bracho, Pereira, & Vásquez, 2008), Logarithmic (Jain & Pathare, 2007) and Two-term (Ait Mohamed et al., 2008). The

mathematical expressions of the selected models are presented in Table 1. The dependent variable of these models, the moisture ratio (MR), was calculated using the mathematical expression of Eq. (3).

3. Quality parameters

3.1. Surface color

Surface color of the samples was measured using a colorimeter (HunterLab, model MiniScan™ XE Plus, Reston, VA, USA). Color was expressed in CIE L^* (whiteness or brightness), a^* (redness/greenness) and b^* (yellowness/blueness) coordinates, standard illuminant D_{65} and observer 10° (Vega-Gálvez, Di Scala, et al., 2009). Ten replicate measurements were performed and results were averaged. In addition, total color difference (ΔE) was calculated using the following Eq. (12), where L_o, a_o and b_o are the control values determined for fresh squid.

$$\Delta E = \left[(a^* - a_0)^2 + (b^* - b_0)^2 + (L^* - L_0)^2\right]^{0.5} \quad (12)$$

3.2. Non-enzymatic browning compounds

The methodology applied for determination of non-enzymatic browning compounds (NEB) dissolved in the rehydration water was that proposed by Vega-Gálvez, Di Scala, et al. (2009). The rehydration water was first clarified by centrifugation at 3200*g* for 10 min. The supernatant was diluted with an equal volume of ethanol (Sigma Chemical CO., St. Louis, MO, USA) at 95% and centrifuged again at 3200*g* for 10 min. The browning index (absorbance at 420 nm) of the clear extracts was determined in quartz buckets using a spectrophotometer (Spectronic® 20 Genesys™, Illinois, USA). All measurements were done in triplicate. NEB was expressed as Abs/g dry matter.

3.3. Rehydration indexes

The dried samples were placed in distilled water at 40 °C for 6 h, using a solid to liquid ratio of 1:50. The samples were then removed, drained for 30 s, and weighed. The rehydration ratio (RR) was calculated according to Eq. (13) and expressed as grams of water absorbed per gram dry matter. The Water Holding Capacity (WHC) was determined by centrifuging the rehydrated samples at 3500*g* for 15 min at 20 °C in tubes fitted with a centrally placed plastic mesh which allowed water to drain freely from the sample during centrifugation. The Water Holding Capacity was calculated from the amount of water removed following Eq. (14), according to previous work (Vega-Gálvez, Di Scala, et al., 2009). All measurements were done in triplicate.

$$\mathrm{RR} = \frac{W_{\mathrm{reh}} \times X_{\mathrm{reh}} - W_{\mathrm{dried}} \times X_{\mathrm{dried}}}{W_{\mathrm{dried}} \times (1 - X_{\mathrm{dried}})} \quad (13)$$

Table 1
Mathematical models selected to simulate jumbo squid drying kinetics.

Model name	Mathematical expression	Eq. number
Newton	$\mathrm{MR} = \exp(-k_1 t)$	(5)
Henderson and Pabis	$\mathrm{MR} = n_1 \exp(-k_2 t)$	(6)
Page	$\mathrm{MR} = \exp(-k_3 t_2^n)$	(7)
Page modified	$\mathrm{MR} = \exp(-(k_4 t)^{n_3})$	(8)
Weibull	$\mathrm{MR} = \exp(-(\frac{t}{\beta})^{\alpha})$	(9)
Logarithmic	$\mathrm{MR} = n_4 + n_5 \exp(-k_5 t)$	(10)
Two-term	$\mathrm{MR} = n_6 \exp(-k_6 t) + n_7 \exp(-k_7 t)$	(11)

$$\mathrm{WHC} = \frac{W_{\mathrm{reh}} \times X_{\mathrm{reh}} - W_l}{W_{\mathrm{reh}} \times X_{\mathrm{reh}}} \times 100 \quad (14)$$

Where W_{reh} is the weight of the sample after the rehydration process, X_{reh} is the corresponding moisture content on a wet basis, W_{dried} is the weight of the sample after the drying process, X_{dried} is the corresponding moisture content on a wet matter and W_l is the weight of the drained liquid after centrifugation.

3.4. Total volatile basic nitrogen

Total volatile basic nitrogen was determined on 5–16 g of minced squid using direct distillation with MgO with a Kjeldahl distillation apparatus and titration according to previous work (Botta, Lauder, & Jewer, 1984). All measurements were done in triplicate.

3.5. Antioxidant activity

Free radical scavenging activity of the samples was determined using the 2,2-diphenyl-2-picryl-hydrazyl (DPPH) method (Turkmen, Sari, & Velioglu, 2005). Different dilutions of the extracts were prepared in triplicate. An aliquot of 2 mL of 0.15 mmol/L DPPH radical in ethanol was added to a test tube with 1 mL of the sample extract. The reaction mixture was vortex-mixed for 30 s and left to stand at room temperature in the dark for 20 min. The absorbance was measured at 517 nm, using a spectrophotometer (Spectronic® 20 Genesys™, Illinois, USA). 80% (v/v) ethanol was used to calibrate the spectrophotometer. Control sample was prepared without adding extract. All solvents and reagents were purchased from Sigma (Sigma Chemical CO., St. Louis, MO, USA). Total antioxidant activity (TAA) was expressed as the percentage inhibition of the DPPH radical and was determined by Eq. (15). All measurements were done in triplicate.

$$(\%)\mathrm{TAA} = \left(1 - \frac{\mathrm{Abs}_{\mathrm{sample}}}{\mathrm{Abs}_{\mathrm{control}}}\right) \times 100 \quad (15)$$

Where TAA is the total antioxidant activity and Abs is the absorbance.

IC_{50}, which is the concentration required to obtain a 50% antioxidant capacity, is typically employed to express the antioxidant activity and to compare the antioxidant capacity of various samples. IC_{50} was determined from a graph of antioxidant capacity (%) against extract concentration (μg /mL).

3.6. Texture

Firmness of samples was measured using a Texture Analyzer (Texture Technologies Corp., TA, XT2, Scardale, NY, USA). The probe was cylindrical with a puncture diameter of 3 mm, a travel distance of 20 mm and 1.7 mm/s test speed. The maximum force was measured by making 1 puncture in each rehydrated squid sample, using 10 slabs per treatment. The mean value of maximum firmness for each treatment was then calculated and the results were expressed as N/mm.

3.7. Statistical analysis

The fit quality of the experimental data to all models was evaluated using the sum square error (SSE, Eq. (16)), root mean square error (RMSE, Eq. (17)) and Chi-square (χ^2, Eq. (18)) statisticals. The effect of air-drying temperature on each quality parameter was estimated using Statgraphics® Plus 5 (Statistical Graphics Corp., Herndon, VA, USA). The results were analyzed by an analysis of variance (ANOVA). Differences among the media were analyzed

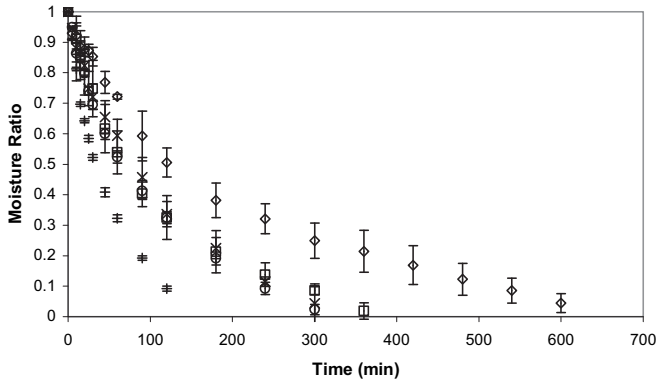

Fig. 1. Effect of air-drying temperature on the drying kinetics of jumbo squid samples: 50 °C (◇), 60 °C (□), 70 °C (×), 80 °C (○) and 90 °C (+). Values are mean ± standard deviation ($n = 3$).

using the least significant difference (LSD) test with a significance level of $\alpha = 0.05$ and a confidence interval of 95% ($P < 0.05$). In addition, the multiple range test (MRT) included in the statistical program was used to demonstrate the existence of homogeneous groups within each of the parameters.

$$\mathrm{SSE} = \frac{1}{N}\sum_{i=1}^{N}(\mathrm{MR_{ei}} - \mathrm{MR_{ci}})^2 \tag{16}$$

$$\mathrm{RMSE} = \left[\frac{1}{N}\sum_{i=1}^{N}(\mathrm{MR_{ci}} - \mathrm{MR_{ei}})^2\right]^{1/2} \tag{17}$$

$$\chi^2 = \frac{\sum_{i=1}^{N}(\mathrm{MR_{ei}} - \mathrm{MR_{ci}})^2}{N - m} \tag{18}$$

4. Results and discussion

4.1. Determination of the effective moisture diffusivity

When applying Eq. (2) for each set of experimental drying data at different air-drying temperatures, the values of effective moisture diffusivity were 0.78, 1.47, 1.43, 1.74 and 3.2 × 10^{-9} m^2/s, for 50, 60, 70, 80 and 90 °C, respectively. These values are within the general range of 10^{-11}–10^{-9} m^2/s for drying of fish reported by Panagiotou, Krokida, Maroulis, and Saravacos (2004). The D_{eff} values mentioned are similar to the corresponding values of tilapia fillets (Medina-Vivanco, Sobral, & Hubinger, 2002) but higher than those reported for Brazilian squid (Teixeira & Tobinaga, 1998), carp (Jain & Pathare, 2007) and shark fillets (Mujaffar & Sankat, 2005). These differences could be explained by seafood species diversity, temperature, muscle orientation, fat content and presence or absence of skin (Medina-Vivanco et al., 2002).

A linear relationship due to the Arrhenius type dependence ($r^2 = 0.88$) was obtained when plotting the natural logarithm of D_{eff} as a function of the reciprocal of absolute temperature. From the slope of this line, an activation energy value of 28.93 kJ/mol was determined, according to Eq. (4).

4.2. Mathematical modeling of the drying curves

Fig. 1 shows the exponential tendency of experimental drying curves for all working temperatures where it is observed that drying time decreases as temperature is increased to reach similar final moisture content. Overlapping of the drying curves at 60, 70 and 80 °C could be explained due to formation of a hardening of the surface area of the squid sample related to the osmotic pre-treatment. This crust presents significant resistance to water migration from within the cell reducing the drying rate (Bellagha, Amami, Farhat, & Kechaou, 2002; Mujaffar & Sankat, 2005). This effect is overcome at high air-drying temperature (e.g. 90 °C) where heat transfer promotes faster evaporation and thus enhances the exits of water vapor by diffusion. When analyzing the effective moisture diffusivity at each temperature, four homogenous groups were found (50 °C, 60–70 °C, 80 °C and 90 °C).

Moreover, drying only occurred in the falling rate period for all the working temperatures justifying the use of the empirical models presented in Table 1. These drying curves behavior was also reported by other authors when working with lobster (Vega-Gálvez, Andres, et al., 2009); sardine (Bellagha et al., 2002) and mackerel (Chavan, Yakupitiyage, & Kumar, 2008). Regression analyses were done for these empirical models by relating the drying time and dimensionless moisture ratio at each drying temperature. Table 2 shows

Table 2
Regression parameters of the mathematical models for each working temperature.

Model	Parameter	Temperature (°C)				
		50	60	70	80	90
Newton	k_1	−0.005 ± 0.001[a]	−0.008 ± 0.0004[a]	−0.009 ± 0.001[a]	−0.037 ± 0.045[a]	−0.019 ± 0.001[a]
Henderson	k_2	−0.005 ± 0.001[a]	−0.008 ± 0.0004[a]	−0.009 ± 0.001[a]	−0.037 ± 0.045[a]	−0.019 ± 0.001[a]
	n_1	0.959 ± 0.013[a]	0.925 ± 0.091[a]	0.961 ± 0.025[a]	1.009 ± 0.050[a]	0.961 ± 0.011[a]
Page	n_2	0.856 ± 0.082[a]	0.919 ± 0.0007[ab]	0.921 ± 0.031[ab]	0.999 ± 0.035[b]	0.971 ± 0.021[c]
	k_3	0.012 ± 0.003[a]	0.016 ± 0.011[ab]	0.013 ± 0.0004[ab]	0.011 ± 0.001[a]	0.023 ± 0.001[b]
Modified page	n_3	0.856 ± 0.082[a]	0.919 ± 0.0007[ab]	0.921 ± 0.032[ab]	0.999 ± 0.035[b]	0.971 ± 0.021[c]
	k_4	0.011 ± 0.00[a]	0.016 ± 0.011[ab]	0.013 ± 0.0004[ab]	0.011 ± 0.001[a]	0.023 ± 0.001[b]
Weibull	α	0.856 ± 0.082[a]	0.919 ± 0.113[ab]	0.921 ± 0.032[ab]	0.999 ± 0.035[b]	0.971 ± 0.021[ab]
	β	191.318 ± 27.010[a]	105.269 ± 20.793[b]	112.174 ± 16.076[b]	93.920 ± 8.608[b]	49.537 ± 1.431[c]
Logaríthmic	n_4	0.930 ± 0.041[a]	0.923 ± 0.060[a]	1.017 ± 0.132[a]	0.972 ± 0.014[a]	0.943 ± 0.011[a]
	n_5	0.042 ± 0.017[a]	0.050 ± 0.025[b]	0.041 ± 0.140[b]	0.003 ± 0.,015[b]	0.051 ± 0.009[b]
	k_5	0.005 ± 0.001[a]	0.010 ± 0.002[b]	0.009 ± 0.003[b]	0.010 ± 0001[b]	0.022 ± 0.001[c]
Two-term	n_6	0.228 ± 0.057[a]	0.415 ± 0.477[a]	0.236 ± 0.222[a]	0.106 ± 0.023[a]	0.156 ± 0.031[a]
	k_5	0.013 ± 0.004[a]	0.051 ± 0.088[a]	0.040 ± 0.030[a]	0.115 ± 0.117[a]	0.072 ± 0.011[a]
	n_7	0.757 ± 0.052[a]	0.585 ± 0.454[a]	0.764 ± 0.231[a]	0.905 ± 0.018[a]	0.855 ± 0.028[a]
	k_6	0.004 ± 0.001[a]	0.006 ± 0.005[ab]	0.008 ± 0.001[ab]	0.009 ± 0.001[b]	0.017 ± 0.0005[c]

Values are mean ± standard deviation ($n = 3$). Values in the same column having the same letter for each parameter are not significantly different at a confidence level of 95%. The k-parameters are expressed in min^{-1}.

Table 3
Statistical tests of the mathematical models selected to simulate jumbo squid drying kinetics.

Tests	Newton	Henderson	Page	Mod. page	Weibull	Logarithmic	Two-term
SSE	0.01243	0.00953	0.00635	0.00635	0.00635	0.00038	0.00032
RMSE	0.00107	0.00094	0.00077	0.000772	0.00077	0.00019	0.00017
χ^2	0.01092	0.01062	0.00717	0.00717	0.00717	0.00049	0.00045

the average values and standard errors of the kinetic and empirical parameters ki ($i = 1, 2, \ldots, 6$), ni ($i = 1, 2, \ldots, 7$), obtained for all the proposed models at the working temperatures. For all kinetic parameters presented in Table 2, an ANOVA of 95% confidence level was performed. When analyzing this table, some parameters increased with air-drying temperature such as k_4 (Modified Page), k_6 (Two-term) and the β-parameter of Weibull ($P < 0.05$). The rest of the parameters did not show least significant differences ($P > 0.05$). These results indicated that there were statistically significant differences, and thus dependence on the drying temperature only for k_4, k_6 and β. The parameters that did not show statistically significant differences probably depend more on the specific characteristics of the material tissue being dried, and possibly on the flow rate of drying air, rather than on process temperature (Mwithiga & Olwal, 2004). Table 3 shows the results of statistical tests (SSE, RMSE and χ^2) performed to the proposed models. These statistical tests evaluate the goodness of fit on the experimental data and they have been reported during food drying studies (Vega-Gálvez, Andres, et al., 2009). The values of mentioned tests were in the range of 0.00032–0.01243 for SSE, 0.00017–0.00107 for RMSE and 0.00045–0.01092 for χ^2. Based on these results, the models that best fitted the experimental data, considering the statistical tests applied, were the Two-term (SSE = 0.00032, RMSE = 0.00017 and $\chi^2 = 0.00044$) followed by the Logarithmic model (SSE = 0.00038, RMSE = 0.01933 and $\chi^2 = 0.00049$). Thus, the mentioned models are suitable to simulate the drying kinetics of jumbo squid. In particular, the good fit of the Two-term model can be related to the presence of its four parameters, which provides a better mathematical approximation on the experimental drying curves. Comparable results were reported by several authors when working with carp (Jain & Pathare, 2007), mackerel (Chavan et al., 2008) and red algae *Gelidium sesquipedale* (Ait Mohamed et al., 2008).

4.3. Surface color and non-enzymatic browning compounds

Color changes are related to the degree of protein structural changes, which cause a difference in the light-scattering properties of the surface of the squid meat as well as browning reactions (Fu, Xue, Miao, Li, & Zhang, 2007; Guizani, Obaid Al-Shoukri, Mothershaw, & Rahman, 2008). In addition, myoglobin is a major contributor to the color of seafood muscle, being the color dependent on both its derivatives and concentration (Guizani et al., 2008). $P < 0.05$ was obtained from the ANOVA on ΔE*, L*,a* and b*. Fig. 2 shows these four chromatic parameters. The redness (a*) and the yellowness (b*) of dried squid meat were significantly higher than fresh meat. The increase in yellowness during drying is an indication of sample browning (Fu et al., 2007). However, lightness (L*) of dried squid meat was slightly lower than fresh squid ($P < 0.05$). Osmotic pre-treatment using NaCl solution significantly affected the lightness of fish meat samples (Fu et al., 2007). Furthermore, when evaluating the chromatic coordinates values during drying, a decrease in these parameters was observed from 50 to 90 °C contributing to the discoloration of the squid samples.

Maillard-type non-enzymatic browning reactions involve the reaction of carbonyl compounds with amino groups. Muscle usually contains carbohydrates in the form of glycogen, reducing sugars, and nucleotides, whereas the amino groups are readily available from the muscle proteins (Rahman, 2006). Squid is rich in proteins and free amino acids, thus, browning is a key problem of quality in this dried product during processing and subsequent storage (Fu et al., 2007). The susceptibility to browning formation, however, differs among squid species as well as process conditions. Fig. 2 presents the color changes of jumbo squid related to non-enzymatic browning reactions. It can be observed that an increase in temperature led to an important formation of brown products. This could be explained due to an increase in the kinetic reaction rate that shows a maximum NEB value of 0.214 ± 0.037 Abs/g dry matter at 90 °C (Rahman, 2006). Furthermore, the effect of water content via decreasing water activity or by plasticizing amorphous systems (dehydrated systems) is a decisive factor in the non-enzymatic browning reaction rate (Acevedo, Schebor, & Buera, 2008).

4.4. Rehydration indexes

Most dehydrated products are rehydrated before use. Rehydration can be considered as an indirect measure of the damage to the material caused by drying and treatment preceding dehydration. The effect of air-drying temperatures on the rehydration indexes of dried jumbo squid meat samples are illustrated in Fig. 3. The Water Holding Capacity (WHC) decreased as the air temperature increased ($P < 0.05$). The maximum WHC was 98.84 ± 0.03 g retained water/100 g water at 50 °C, which implies that this drying temperature causes tissue structure damage; thus, the squid sample dehydrated at this temperature retained a great amount of water. On the other hand, samples dried at 80 and 90 °C have reduced their WHC, thereby preventing the complete rehydration of the dried product. Similar investigations reported that air-drying temperature is the main factor affecting the WHC (Vega-Gálvez, Di Scala, et al., 2009). In the same figure, it can be observed that the rehydration ratio (RR) was affected by the drying temperatures,

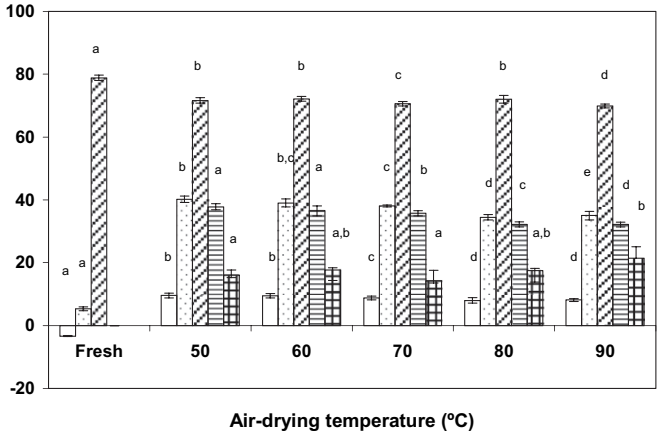

Fig. 2. Effect of air-drying temperature on color differences (ΔE), chromatic coordinates L*, a*, b* and non-enzymatic browning (NEB) of fresh and dry-rehydrated jumbo squid samples. Identical letters above the bars indicate no significant ($P < 0.05$). NEB $\times 10^{-2}$. Key: a*, b*, L*, ΔE, NEB. Bars represent mean ± standard deviation ($n = 3$).

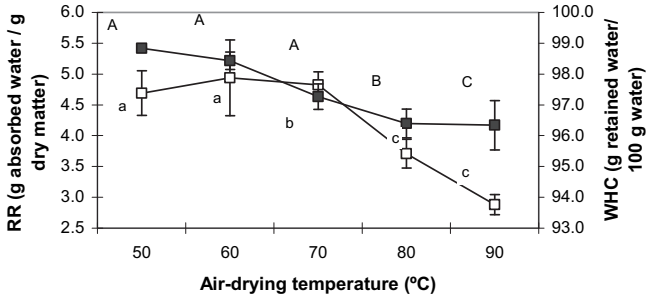

Fig. 3. Effect of air-drying temperature on the rehydration ratio (RR) and the water holding capacity (WHC) for dry-rehydrated jumbo squid samples. Identical letters above the bars indicate no significant ($P < 0.05$). (−□− : RR, −■− : WHC). Values are mean ± standard deviation ($n = 3$).

since absorbed water decreased with drying temperature ($P < 0.05$). The lowest RR value was 2.88 ± 0.16 (g absorbed water/g dry matter) at 90 °C. Moreover, it is generally accepted that the degree of rehydration is dependent on the degree of cellular and structural disruption (Guizani et al., 2008). Thus, variations in rehydration indexes values between samples revealed a degree of reducing space between both groups of muscle fibers and individual fibers as well as by a progressive reduction in muscle fiber diameter (Guizani et al., 2008).

4.5. Total volatile basic nitrogen

Total volatile basic nitrogen (TVBN) routinely has been used worldwide as indicator of fish quality (Doe, 2000; Pivarnik, Ellis, Wang, & Reilly, 2001). Initial value of squid TVBN was 14.67 ± 0.10 mg/100 g sample, this value is comparable to those reported for fresh seafood by other authors (Pivarnik et al., 2001; Quitral Robles et al., 2003). Table 4 shows the values of TVBN for the fresh and osmo-dried squid samples. It can be seen that process temperature increased considerably the amount of nitrogen due to an increase in free volatile compounds during thermal processing. Similar results were found by other authors working with horse mackerel (Shi et al., 2008). Quitral Robles et al. (2003) reported a decrease on TVBN above 80 °C during thermal treatment of mora squid applying different combinations of time–temperature.

The values of TVBN reported in this investigation are in the range of 29.38–73.68 mg N/100 g sample when the samples were dehydrated from 50 to 90 °C (Table 4). The process temperatures of 80 °C and 90 °C resulted in TVBN values higher than 60 mg/100 g, which is a limit established by the Chilean Food Sanitation Regulations (Quitral Robles et al., 2003). However, squid has an intrinsically great concentration of the salt ammonium chloride (NH_4Cl) which is dissolved in the cellular medium at an acid pH. During determination of TVBN the squid samples were immersed in an alkaline ambient, the NH_4Cl becomes into ammonium hydroxide and then ammonia. Therefore, the last compound is not a product of microbial protein decomposition but the result of the decomposition of NH_4Cl in alkaline media. This reaction is inevitably a forced pathway in the determination of TVBN with this methodology. Moreover, the squid size is an important factor that affects directly its ammonia content. Big sized squid (adults) samples were related to high contents of TVBN (from 70 to 270 mg N/100 g sample), (Albretch, 2006). However, it was reported that the acceptable limit of squid TVBN was dependent on the species, environment and physiological conditions, processing and storage conditions and thus, highly variable (Fu et al., 2007; Quitral Robles et al., 2003).

4.6. Antioxidant activity

The radical scavenging activity was investigated based on air-drying temperature ($P < 0.05$) as observed in Table 4. It can be seen that this process variable has an important effect on antioxidant activity (AA) of the squid samples. All treatments showed a decrease in the AA when related to the initial value. In fact, high temperature (e.g. 90 °C) showed the lowest value of AA compared to the other drying temperatures. Treatments at 50 and 80 °C resulted in similar behavior perhaps due to equivalent time–temperature processes. The antioxidant activity in fish products has been related to product proteins. In particular, peptides from a variety of high-protein sources have been reported to show antioxidant effects (Jongberg, Carlsen, & Skibsted, 2009). Nevertheless, the structure–activity relationship and the antioxidant mechanism of active peptides have not yet been fully elucidated and the antioxidant activity has been related to the amino acid composition and sequence of the different peptides released during processing (Jongberg et al., 2009).

4.7. Texture

Texture is one of the most important sensory characteristics that affect overall quality of fresh fish. It is usually correlated to rheological parameters obtained by mechanical measurements, which are very important in understanding the structure of food and how it is affected by the drying process (Telis & Telis-Romero, 2005). In this investigation, firmness, i.e. the maximum force applied to puncture the squid tissue, was measured as an indicator of texture. Table 4 shows the effects of air-drying temperature on the squid firmness for both fresh and dried-rehydrated samples ($P < 0.05$). It can be observed that an increase in air-drying temperature has an important influence on this textural property. All drying treatments showed an increase in this property compared to the fresh sample, indicating lost of tenderness, a sensory characteristic different from the fresh product. Comparable results were reported when cooking squid mantles in water (Otwell & Hamann, 1979) and during shrimp drying (Yuvanaree, Warunee, Sakamon, & Somchart, 2004).

These modifications in the squid texture could be related to protein denaturation during the thermal processing since the protein matrix in muscle has marked effect upon its functionality and properties (Perera, 2005; Rahman, 2006). Thermal denaturation temperatures of fish muscle proteins were observed between 40 and 80 °C (Kong, Tang, Rasco, & Crapo, 2007). When analyzing the

Table 4
Effect of air-drying temperature on total volatile basic nitrogen (TVBN), antioxidant activity (IC_{50}) and firmness of jumbo squid.

Quality parameter	Fresh	Temperature (°C)				
		50	60	70	80	90
TVBN (mg N/100 g sample)	14.67 ± 0.10^{a}	29.38 ± 0.10^{b}	36.56 ± 0.83^{c}	59.39 ± 2.22^{d}	63.51 ± 2.56^{e}	73.68 ± 3.33^{f}
IC_{50} (μg/mL)	1767.32 ± 19.13^{a}	13 709.55 ± 683.71^{b}	1775.35 ± 401.36^{c}	15 792.74 ± 140.45^{d}	14 049.77 ± 130.86^{b}	20 575.17 ± 145.42^{e}
Firmness (N/mm)	0.88 ± 0.17^{a}	1.45 ± 0.20^{bc}	1.60 ± 0.25^{c}	1.53 ± 0.25^{bc}	1.33 ± 0.28^{b}	1.44 ± 0.28^{bc}

Values are mean ± standard deviation ($n = 3$). Identical letters indicate no significant ($P < 0.05$).

quantity of squid proteins remaining after the dehydration process, retentions of 77.33 g/100 g dry matter (50 °C), 80.15 g/100 g dry matter (60 °C), 84.80 g/100 g dry matter (70 °C), 85.31 g/100 g dry matter (80 °C) and 98.31 g/100 g dry matter (90 °C) was observed. Thus, further study is needed to fully understand the mechanisms involved, e.g. employing differential scanning calorimetry (DSC) analysis and microscopic examination of collagen and muscle fibers might help reveal the mechanisms involved in the nature of these protein changes that occur during drying (Kong et al., 2007).

5. Conclusions

To simulate the drying behavior of squid, seven different thin-layer drying models were compared. Based on the statistical tests results, the Logarithmic and Two-term drying models gave the best fits and could be used to accurately predict the moisture content of dried squid from 50 to 90 °C. Air-drying temperature influenced the chemical, physical and nutritional properties of squid. Discoloration of product was more noticeable at high drying temperatures where combined effects of non-enzymatic browning as well as protein denaturation modified the original color of the squid samples. Rehydration indexes (RR and WHC) showed a decrease while texture presented an increase with increasing air-drying temperature probably due to changes in food protein matrix. The important increase of Total volatile basic nitrogen (TVBN) with air-drying temperature could be associated to the salt ammonium chloride decomposition during determination of TVBN, in particular at high temperatures (e.g. 80 and 90 °C). The antioxidant activity presented a decrease with process temperature, in particular at high process temperatures (e.g. 90 °C). In conclusion, the results of this work indicate that the drying kinetics together with the reported quality attributes of the dried squid can be used to improve the final characteristics of the product. Optimization of food quality during process requires more investigations in order to overcome the constraints related to structural and functional food behavior and their role in the coupling of heat and mass transfer mechanisms.

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