DRYING CHARACTERISTICS AND KINETICS OF LOVASTATIN DEGRADATION OF OYSTER MUSHROOM (*PLEUROTUS OSTREATUS*) SLICES

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***Abstract*— Oyster mushroom slices were dried using hot air dryer. The lovastatin content in oyster mushroom slices during drying was evaluated at 45, 55 and 65˚C. The first-order reaction model adequately described degradation of lovastatin. In this study, the modeling of the drying process was also performed. Four mathematical models were fitted to the experimental data. The performance of these models is evaluated by comparing the coefficient of determination, root mean square error and reduce chi-square between the observed and predicted moisture ratio. The Page model gave the best results for describing drying of oyster mushroom slices.**

***Keywords*— Drying; Kinetic; Lovastatin; Modeling; Oyster mushroom.**

I. INTRODUCTION

Pleurotus mushrooms, commonly known as oyster mushrooms, grow wildly in tropical and subtropical areas, and are easily artificially cultivated. They are healthy foods, low in calories and in fat, rich in protein, chitin, vitamins and minerals (Akindahunsi and Oyetayo, 2006; Mattila *et al*., 2002). Mushrooms are thought to be beneficial for such diseases as hypertension, hypercholesterolemia, and cancer (Bobek and Galbavy, 1999; Borchers *et al*., 2004). Edible mushrooms are always available in fruiting bodies form for cooking whereas medicinal mushrooms are always available in mycelia due to their rare and expensive nature. Oyster mushroom contains lovastatin, an inhibitor of cholesterol biosynthesis (Gunde-Cimerman *et al*., 1993) which has (similarly to other statins with hypocholesterolemic activity) simultaneously antioxidative properties (Hoffman *et al.*, 1992). Lovastatin is known to be produced by *Monascus* species and is one of statins (3-hydroxy-3-methylglutaryl coenzyme A reductase inhibitors), which inhibit the rate-limiting enzyme in the production of cholesterol, lower total and LDL cholesterol levels and have been proven to reduce the risk of coronary heart disease. These statins have been shown to have effectively anti-inflammatory, antioxidant and profibrinolytic properties and to prevent acute coronary syndromes and atherosclerotic disease (Aarons *et al*., 2007).

Drying is a complex thermal process in which unsteady heat and moisture transfer occur simultaneously (Doymaz, 2012). From an engineering point of view, it is important to develop a better understanding of the controlling parameters of this complex process. Mathematical modeling is the best and appropriate approach for describing the kinetics of the drying process. Precise modeling of the behavior of drying of agricultural products requires specific correlation and regression statistical methods in order to attain a set of equations that give an accurate explanation of the process (Celma *et al*., 2008). Many mathematical models have proposed to describe the drying process, of them, thin-layer drying models have been widely in use. These models can be categorized as theoretical, semi-theoretical, and empirical (McMinn, 2006).

The mushrooms of the Pleurotus genus are delicate and sensitive. For high moisture content and rich nutrients, oyster mushrooms spoil easily and quickly. After harvesting, the self-life of fresh mushrooms is only about 22 hour at ambient temperature. In refrigerator storage system, it can be stored 6–9 days (Mustayen *et al.*, 2015). Various physiological and morphological changes occur after harvesting which makes the mushrooms unacceptable for consumption. Browning, weight loss, and microbial spoilage are the most common postharvest changes in mushrooms which often result in enormous economic losses (Tolera and Abera, 2017). So preservation of oyster mushroom topic is very important. To extend the availability and shelf life of oyster mushrooms, processing methods such as sun drying, hot air drying, solar drying, vacuum and freeze drying are recommended. The dried product offers, increased shelf life and pleasant flavor and also increase the potential for storage and transport of the product (Dunkwal *et al*., 2007). In several reports the nutritional aspects of cultivated and wild edible mushroom have been studied (Manjunathan and Kaviyarasan, 2011; Ouzouni *et al*., 2009). Different drying methods are believed to impact on chemical composition, physico-chemical properties and antioxidant activities of the mushrooms (Ma *et al*., 2013; Muyanja *et al*., 2014). But no scientific work has been reported yet on the degradation kinetics of lovastatin in oyster mushroom drying. Drying temperature and time are two major factors influencing the degradation kinetics of lovastatin. The objectives of this study were to (1) observe the effect of drying temperature on drying characteristics of oyster mushrooms, (2) select the best mathematical model for the drying curves and (3) determine the degradation kinetics of lovastatin during hot air drying at temperatures varying from 45 to 65°C.

II. METHODS

A. Material

Oyster mushroom (*Pleurotus ostreatus*), which is rich in bioactive components, has been used in drying experiments. The mushrooms, selected with the care of being visually fresh and of the same maturity level, have been obtained from a local producer in a town of Pamukkale, Denizli. They were taken in polyethylene packages and stored at 4 ± 0.5°C in a refrigerator until drying. Moisture content of the samples was determined in a vacuum oven (Model JSVO-60T, JSR) at 70°C for 24h (AOAC, 1990). The initial moisture content of oyster mushroom samples was 84.48±0.5%.

B. Drying Procedure

The drying process of the oyster mushroom was carried out by a cabinet dryer (Yücebaş Makine Ltd. Inc. İzmir, Turkey) at 45, 55 and 65 C. At all temperatures, a constant airflow of 0.2 m/s and a constant 20% relative humidity was used during drying. The cabinet dryer was described previously by Demiray and Tulek (2012). The temperature and relative humidity of the cabinet dryer were stabilized for an hour. After the dryers reached steady-state conditions, the samples were samples were taken out of refrigerator and kept until room temperature. Later oyster mushrooms were washed and sliced in thickness of 6.5 ± 1 mm using a sharp knife. Moisture loss during the drying process was recorded at 15 min interval, and the weight of the oyster mushroom slices was measured by an analytical balance (Denver Instrument, TP-3002, Germany) with an accuracy of 0.01 mg. Dried samples were wrapped in aluminum foil in polyethylene packages and stored at –20°C for further lovastatin analyses. Drying was stopped when the moisture content of the sample was reduced to 10% (wet basis). All experiments were carried out in triplicates.

C. Mathematical Modeling of Drying Curves

The experimental drying data of oyster mushroom slices at different temperatures were fitted into 5 commonly used thin-layer drying models, listed in Table 1. In these models, MR is the dimensionless moisture ratio which is calculated using Eq. (1).

$$MR = \frac{M - M_e}{M_i - M_e} \tag{1}$$

where MR is the moisture ratio, M is the moisture content at a specific time (kg water kg^{-1} dry matter), M_i is the initial moisture content (kg water kg^{-1} dry matter), M_e is the equilibrium moisture content (kg water kg^{-1} dry matter) (Demiray and Tulek, 2012).

Nonlinear regression was used to obtain each constant of the selected mathematical models. Moreover, the criteria such as coefficient of determination (R^2), reduced chi-square (χ^2) and root mean square error (RMSE) were calculated to evaluate the fitting of a model to experimental data. The highest values of R^2, lowest values of χ^2 and RMSE which are the closest to zero, were chosen for goodness of fit. These parameters can be calculated as below

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

$$\chi^2 = \frac{\sum_{i=1}^{N} \left(MR_{\exp,i} - MR_{pre,i} \right)^2}{N - z} \tag{3}$$

where $MR_{exp,i}$ and $MR_{pre,i}$ are the experimental and predicted moisture ratios, respectively. N is the number of observations and z is the number of constants (Akpinar, 2006).

D. Lovastatin Analysis

For the extraction of lovastatin, the method suggested by Li *et al.* (2004) was used with some modifications. Two grams of fresh or dried oyster mushroom samples were weighed to a polypropylene centrifuge tube and extracted with 20 mL of ethanol-acetonitrile solution (4:3, v/v) for 60 min on an ultrasonic bath and subsequently centrifuged (Universal 30RF, Hettich Zentrifugen, Tuttlingen, Germany) for 20 min at 9000 rpm. This extraction procedure was repeated three times, and the total supernatant was transferred to an amber bottle which volume is 25 ml. The final solution was kept standing for 30 min, and then filtered through 0.45 µm membrane filters (Minisart, Sartorius, Germany) before injection into the HPLC equipment.

Lovastatin contents of fresh and dried oyster mushroom samples were determined by a Shimadzu brand HPLC unit (Shimadzu LC-20AD, Shimadzu Corporation, Kyoto, Japan) equipped with a quaternary pump system (LC-20A), a photodiode array detector (SPD-M20A), a degasser (DGU-20A) and a column oven (CTO-20A). Chromatograms were analyzed with the "LCsolution" software program. A Kromasil 300-5 C18 column (250 × 4.6 mm, ID, 5 µm) was used with the isocratic elution of mobile phase containing a mixture of acetonitrile:water (70:30, v/v) at a flowrate of 0.50 mL/min at 30˚C. Injection volume was 20 mL while detection wavelengths were 237 nm for lovastatin. Recovery rates were found higher than 90%. Retention times and UV-vis spectra of pure lovastatin was used to identify peaks in sample chromatograms.

E. Kinetic Parameters

The degradation of lovastatin during drying at 45, 55 and 65 ˚C, was modeled by Eqs. (4) - (5) for a zero and first-order reaction, respectively:

$$C = C_0 + k_0 t \tag{4}$$

Table 1. Mathematical models applied to drying curves of oyster mushroom slices.

Model Name	Model	Reference
Logaritmic	MR = $a$exp(-kt) + c	Toğrul and Pehlivan, 2003
Lewis	MR = exp(-kt)	Doymaz, 2006
Henderson and Pabis	MR = $a$exp(-kt)	Evin, 2011
Page	MR = exp(-kt^n)	Wang *et al*., 2007

$$\ln C = \ln C_0 \pm k_1 t \quad (5)$$

where C is the concentration of lovastatin at any given drying time, C_0 is initial values of untreated samples and k_0 is the zero order rate constant, k_1 is the first order rate constant (min^{-1}). t is the drying time (min). The efficacy of fitted model was determined by the highest correlation coefficient (R^2).

The Arrhenius equation is the most widely accepted method of accounting for the temperature dependence of the rate constant in food systems. Temperature dependence of lovastatin degradation was determined by the Arrhenius equation (Eq. (6)):

$$k = k_a \exp(-\frac{E_a}{RT}) \quad (6)$$

where k is the rate constant at absolute temperature T (K), k_a is the frequency factor, E_a is the activation energy (kJ/mol), and R is the universal gas constant (8.314 J/(molK)).

The coefficient Q_{10} is another way to characterize the effect of the temperature on the rate of a reaction and it was calculated by the Eq. (7).

$$Q_{10} = (k_2/k_1)^{10/(T_2-T_1)} \quad (7)$$

where k_1 and k_2 are reaction rate constants at temperatures T_1 and T_2, respectively.

The experimental results are expressed as mean ± standard deviation of triplicate measurements and results were processed using Microsoft Excel.

III. RESULTS and DISCUSSIONS

A. Effect of drying temperature on drying kinetics of oyster mushroom slices

Figure 1 shows the change in moisture content of oyster mushroom slices with time by hot air drying. It is clear that the moisture content decreases continuously with drying time. As expected, drying temperatures had much stronger effect on the drying moisture content of oyster mushroom slices. The temperature influence was higher at 65˚C drying temperature. A constant rate period was not observed in any of the experiments of this work, so the entire drying process for oyster mushroom occurs in the range of the falling rate period. The results were generally in agreement with some literature studies on drying of various fruits and vegetables such as tomato (Doymaz, 2007), mushroom (Tulek, 2011), onion (Demiray *et al.*, 2017), apricot (Faal *et al.*, 2015) and carrot (Doymaz, 2017).

To describe hot air drying kinetics of oyster mushroom slices, four different semi-empirical thin layer drying models were used, and among these models Page model was observed as the most appropriate for all experimental data with values for the coefficient of determination of greater than 0.9849 and the chi-square and RMSE of estimates lower than 0.00090 and 0.020333, respectively, as given in Table 2. Similar results were obtained by some authors on drying of various fruits and vegetables (Horuz and Maskan, 2015; Rojas and Augusto, 2018; Adiletta *et al.*, 2016).

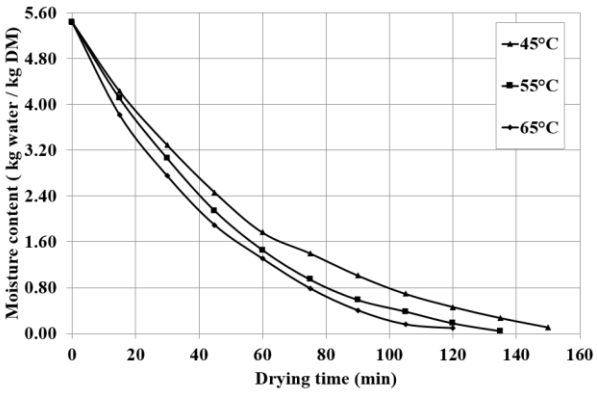

Figure 1. Effect of drying temperature on moisture content for oyster mushroom slices.

Table 2. Statistical results obtained from the selected models.

Model	Temperature (°C)	χ^2	RMSE	R^2
Lewis	45	0.0137	0.1172	0.946
	55	0.0150	0.1226	0.968
	65	0.0142	0.1193	0.958
Page	45	0.0002	0.0153	0.990
	55	0.0009	0.0091	0.996
	65	0.0004	0.0203	0.984
Henderson and Pabis	45	0.0056	0.0714	0.958
	55	0.0711	0.0056	0.980
	65	0.0074	0.0813	0.971
Logarithmic	45	0.0043	0.0595	0.968
	55	0.0217	0.1318	0.925
	65	0.0242	0.1373	0.905

B. Kinetics of lovastatin degradation

The degradation of lovastatin during drying of oyster mushroom slices was studied in terms of lovastatin concentration. During drying, lovastatin concentrations in all samples were gradually decreased with time at a rate depending on the drying temperature. The degradation of lovastatin in all samples fitted by zero-order and first-order kinetics models was shown in Fig. 2 and Fig. 3, respectively. The analysis of this figures show that the degradation of lovastatin follows first-order reaction kinetics with respect to temperature because the curves are linear than zero-order reaction models curves. Besides the results showed that the first-order reaction described experimental data of lovastatin degradation during drying very well with higher R^2 intervals (R^2 = 0.985-0.991) as compared with zero-order reaction. This result agreed well with the finding of Ou *et al*. (2009) who found that the thermal degradation of lovastatin in red yeast rice solution at 90 – 121˚C followed a first-order reaction from using simple kinetics model. The reaction rate constants (k) increased as the drying temperature increased. The k values of first-order reaction were within the range of 0.0092-0.0184 min^{-1} (Table 3).

The temperature dependence of rate constant was simulated by Arrhenius equation (Eq. 6). Activation energies (E_a) were then estimated from slope of ln k on $1/T$ plot by regression analysis according to the Eq. 2. Fig. 4 presents this plot, and the E_a calculated was 30.95

Table 3. The kinetic parameters for *lovastatin* losses in oyster mushroom slices during drying at different temperatures.

	Temperature (°C)	Zero-Order Model				First-Order Model			
		k_0	R^2	Q_{10} *value*	E_a (kJ mol^{-1})	k_1 (min^{-1})	R^2	Q_{10} *value*	E_a (kJ mol^{-1})
Lovastain	45	0.542	0.9679	1.21	15.65	0.0092	0.9849	1.42	30.95
	55	0.653	0.9708			0.0131	0.9885		
	65	0.769	0.9002	1.18		0.0184	0.9910	1.41	

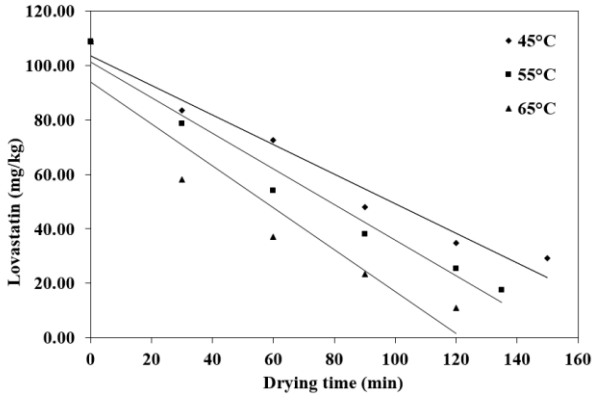

Figure 2. Zero-order kinetic reaction model of lovastatin degradation of oyster mushroom slices as a function of drying time at different drying temperatures.

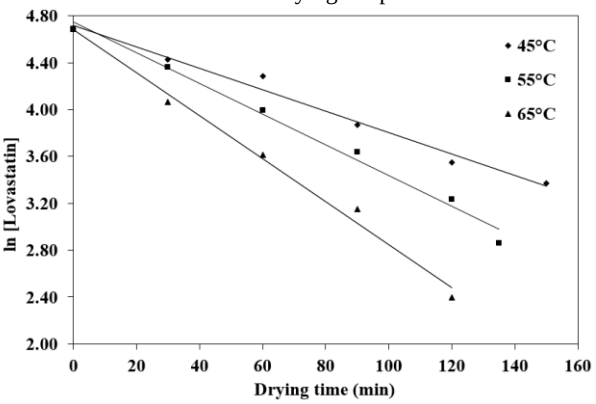

Figure 3. First-order kinetic reaction model of lovastatin degradation of oyster mushroom slices as a function of drying time at different drying temperatures.

kJ/mol. Higher activation energy indicated that a small temperature change affected to degrade a specific compound more rapidly. Blasco *et al.* (2004) found a value of E_a for the ascorbic acid in mushroom *(Agaricus bisporus*) around 46.36 kJ/mol. This indicates that the lovastatin degradation in mushroom is more durable to temperature elevation than ascorbic acid.

Table 3 presents the values of Q_{10} for the temperatures used in this study. The highest value is obtained within the range of 45 to 55˚C, indicating that in this range the degradation kinetic was strongly affected by the drying temperature. In other words, increasing drying temperature from 45 to 55˚C increased the reaction rate of lovastatin degradation in mushrooms by about 1.42 times. The results indicated that the drying temperature of 45˚C is more suitable to minimize the degradation of lovastatin in mushroom slices during hot air drying.

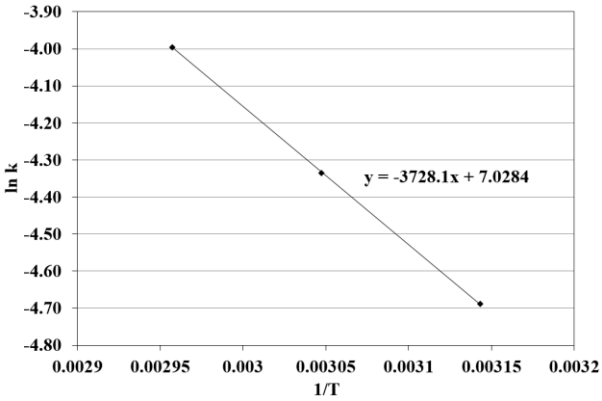

Figure 4. The Arrhenius plots of lovastatin degradation relating rate constants of drying temperatures.

IV. CONCLUSIONS

Drying kinetics of oyster mushroom slices was investigated in hot air dryer, at constant air velocity of 0.2 m/s and a temperature range 45 – 65˚C and a relative humidity 20%. Samples did not observe a constant rate period of drying under the experimental conditions employed and showed only a falling rate period like most food products. Page model, which gave higher correlation coefficient and lower reduced Chi-square and root means square error, were considered the best for explaining the drying oyster mushroom slices. The kinetics of lovastatin degradation of oyster mushroom slices followed a first-order reaction. The rate constant increased with temperature and the dependence could be described using the Arrhenius equation. The activation energy value for lovastatin was 30.95 kJ mol^{-1}. The highest Q_{10} value for lovastatin was calculated at increasing drying temperature from 45 to 55°C.

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