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ORIGINAL RESEARCH PAPER

TEMPERATURE INFLUENCE ON THE *AGARICUS BISPORUS* MUSHROOMS DEHYDRATION PROCESS

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Abstract: Edible mushrooms are foods with high nutritional value, delicious and therapeutic products. The main objective of this research was to investigate the influence of different temperatures of the dehydration process on the microstructure and color of *Agaricus bisporus* mushrooms. Tray drying conditions were: constant air velocity, 50, 60 and 70 °C suited to relative humidity (RH) values of 12.17, 4.8 and 2.26 % respectively. Mathematical modeling of drying process, effective moisture diffusivity and activation energy calculations were presented. The effective moisture diffusivity was between $(1.09665 – 2.11723)\cdot10^{-10}$ $m^2\cdot s^{-1}$ for white and $(0.99522 – 1.69885)\cdot10^{-10}$ $m^2\cdot s^{-1}$ for brown mushrooms. The activation energy values indicate a higher energy input for the white mushrooms drying. SEM micrographs revealed the overall integrity of the tissue and some hyphae from the stipes of brown and white mushroom appeared intact and similar. At 70 °C, the presence of these crystals is more emphasis due to calcium.

Keywords: *activation energy, color, convective air drying, effective moisture diffusivity, texture*

INTRODUCTION

Spread all over the world, fungi have almost 200 000 species, subspecies and varieties. It is estimated that there are about 140 000 mushroom species on earth and only 22 000 of these are known [1]. Until now a number of 2000 mushroom species are reported in Romania [2]. Production quantity of mushrooms and truffles in Romania was 9.3×10^6 kg in 2013 and 8.785×10^6 kg in 2014 according to [3], data published on February 2015.

Mushrooms are one of the useful, delicious and consumed food products [4]. Edible mushrooms are considered food with a high nutritional value and some of them are therapeutic [5]. It is relevant that the mushrooms contain combinations of protein, carbohydrates, minerals and vitamins [6].

Edible mushrooms contain fibers and some nutrients that have medicinal aspects; also they are poor source of carbohydrates and for this reason they can be included in the diet of people with diabetic disorder [7]. The chitin content depends by the kind and type of mushroom and according to [8] the chitin content in *Agaricus bisporus* is higher than in *Pleurotus*.

Mushrooms are a seasonal and highly perishable with about 90 % (wet basis) moisture [9] which needs to be reduced to an acceptable value so as to avoid microbial growth. Drying is a complicated process with simultaneous heat and mass transfer, and food drying is especially a very complex process because of the differential structure of products.

Drying offers a means of preserving foods in stable and safe conditions, as it reduces the water activity and extends shelf-life much longer than that of fresh fruits and vegetables. Anyway some several modifications on physical, structural, chemical transformations can occur with changes in color, texture, odor or other properties of the solid product. The total energy consumption is 10 - 15 % of the total energy consumption in all industries, but the methods of drying are various using more than 200 types of dryers [10]. So, many conventional thermal methods, including hot-air drying, vacuum drying, and freeze-drying, occur in low drying rates in the falling rate period of drying [11 – 13]. The most common drying method employed for food materials is hot air drying, which is the simplest and most economical among the various methods.

Literature present many mathematical models of drying considering the drying of foods products in one layer or thin layer of sample particles or slices [14] due to their ease to use and less data requiring [10].

The objectives of this study were to investigate the effect of temperature on tray drying kinetics and to evaluate the quality parameters (texture and color) of dried mushrooms. The kinetic parameters that describe the diffusion process in terms of moisture diffusivity and activation energy were estimated.

MATERIALS AND METHODS

Raw material

Fresh white button and brown strain mushrooms *Agaricus bisporus* were purchased from a local supermarket, in Galati, Romania. Slices of 5 mm thickness were obtained

by cutting mushrooms vertically with an electric slicer (Philips HR7762/91). Without any pre-treatment slices were dehydrated in a pilot plant tray drier (UOP8MkII model 2014, Armfield Ltd., England).
The tray drier has capacity up to 2.1 kg of wet material and it is integrated with a full data logging to control the flow rate, temperature (up to 80 °C), humidity, air velocity (from 0.4 to 3.0 $m \cdot s^{-1}$) and to determine drying rate.
The software includes PID (Proportional Integral Derivative) controller of air temperature before the trays and user-defined control of air velocity [15].
Drying experiments were performed considering constant air velocity 0.55 $m \cdot s^{-1}$ and three different temperatures 50, 60 and 70 °C and correspondent relative humidity (RH) 12.17, 4.8 and 2.26 % respectively.

Mathematical modeling of tray drying curves

For the mathematical modeling, we assumed the thin layer drying equations which are suitable for drying as on layer of sample particles or slices [14]. If the relative humidity of the drying air is constant during the drying process, then the moisture equilibrium is constant too [10].
The moisture ratio (*MR*) of slices of white button and brown mushrooms was calculated using the following equation:

$$MR = \frac{M_t - M_e}{M_0 - M_e} \tag{1}$$

where: M_t is mean moisture content at time t (% dry basis); M_e is equilibrium moisture content (% dry basis); M_0 is initial moisture content (% dry basis).

Effective moisture diffusivity calculation

Diffusion in solids during drying is a complex process that may involve molecular diffusion, capillary flow, Knudsen flow, hydrodynamic flow, or surface diffusion [10]. All these phenomena are combined in effective moisture diffusivity that can be calculated from linearity of MR versus time (equation 2):

$$\ln(MR) = \ln(a) - k \cdot t \tag{2}$$

where: a is mean the constant (dimensionless), t is the drying time (s) and k is the drying constant (s^{-1}).
The drying constant, k is defined as:

$$k = -\frac{\pi^2 \cdot D_{eff}}{A_2} \tag{3}$$

where:

$$A_2 = 4 \cdot L^2 \tag{4}$$

In this case D_{eff} can be estimated from drying constant k with eqn. (5):

$$D_{eff} = -\frac{A_2 \cdot k}{\pi^2} \tag{5}$$

where: A_2 is mean the geometric constant (m^2); L is the thickness of the slice if drying occurs only from one side (m); D_{eff} is the effective moisture diffusivity ($m^2 \cdot s^{-1}$).

Activation energy calculation

The effect of different drying temperatures on D_{eff} is described by Arrhenius equation that indicate a linear variation of ln (D_{eff}) versus [1/(T+273.15] (equation 6).

$$\ln(D_{eff}) = \ln(D_0) - 10^3 \cdot \frac{E_a}{R} \cdot \frac{1}{(T + 273.15)} \quad (6)$$

where: D_0 is mean the Arrhenius factor or the reference diffusion coefficient at infinitely high temperature ($m^2 \cdot s^{-1}$); E_a is activation energy ($kJ \cdot mol^{-1}$); R is the universal gas constant (8.314 $kJ \cdot mol^{-1} \cdot K^{-1}$); T is absolute temperature (K).

The slope of equation 6 is equal to ($-10^3 \cdot Ea/R$), so E_a is easily calculated with revealing the slope by deriving from linear regression of ln(D_{eff}) – [1/(T+273.15].

Microstructure

A scanning electron microscope (SEM) (Quanta 200 model, Fei Co., Netherlands) operating at an acceleration voltage of 10 kV was used to examine the microstructure of fresh and dried white button and brown *Agaricus bisporus* mushrooms.

The samples were fixed on aluminum stub using carbon doubled adhesive tape. To create a conductive surface useful for a higher resolution micrograph, the cross-sectioned mushroom surfaces were sputter-coated with a gold-palladium alloy thin layer, prior to the SEM analysis.

The metallization was carried out using a sputtering device (SPI Supplies, U.S.A.) for 120 s at 18 mA obtaining 5 nm as thickness.

In order to highlight the effect of time, temperature and thermal treatment method on the microstructure of white and brown mushrooms, the SEM analysis was performed in both regions as pileus and interior tissue.

Color measurement

Color measurements (before and after drying process) were performed using a Chroma Meter (Konica Minolta colorimeter CR-400 model, 2015) according to the [9, 16]. The colorimeter uses three values (*L, a* and *b*) to describe the precise location of a color inside a three-dimensional visible color space and before each actual color measurement was calibrated against standard white plate.

The measuring surface included the cap, gills and stipe. The measurements were displayed in *L, a* and *b* values which represents light–dark spectrum with a range from 0 (black) to 100 (white), the green–red spectrum with a range from - 60 (green) to + 60 (red) and the blue-yellow spectrum with a range from - 60 (blue) to + 60 (yellow) dimensions respectively.

An increasing *L* value indicates a higher degree of whiteness. Total color difference was calculated using equation 7, where subscript "0" refers to the color reading of fresh mushroom.

Fresh mushroom was used as the reference and a larger ΔE denotes greater color change from the reference material [17].

$$\Delta E = \sqrt{(L_0 - L)^2 + (a_0 - a)^2 + (b - b_0)^2} \quad (7)$$

where: L is mean degree of lightness to darkness; L_0 is the initial value of L; a is the degree of redness to greenness; a_0 is the initial value of a; b is the degree of yellowness to blueness; b_0 is the initial value of b. All these parameters are dimensionless.
All color measurements were performed in duplicate at different positions of samples.

RESULTS AND DISCUSSION

Drying kinetics

The tray dryer is integrated with a data logging UOP8MkII-306 software which allows registration of the drying parameters and performs some standard calculations on the data.
The experiments were performed at the equilibrium moisture content 4.0837 ± 0.46 %.
Figure 1 presents how the moisture ratio depending on temperature varies in time, at constant air velocity (0.55 $m \cdot s^{-1}$) in the tray drier for both mushrooms types.
Increasing the air temperature from 50 to 70 °C, the drying rate loss increased and the drying time decreased (from 250 min at 50 °C up to 130 min at 70 °C).

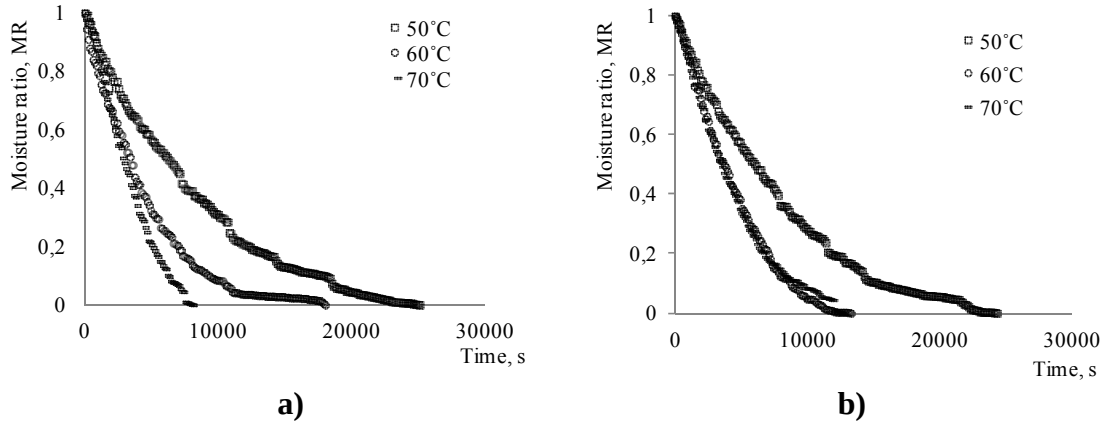

Figure 1. *Effect of drying parameters on MR for white button (a) and brown (b) slices of mushroom*

The initial moisture content of the slices of mushrooms was 92.89 ± 1.5 % and the rate of moisture loss was high in the range of 0.727 - 0.505. Most part of the moisture was lost during the first period where sensible heat is transferred to the product directly influencing the moisture content and increasing the rate of water evaporation.
Drying curves of mushrooms slices exhibited a fast drying rate at the beginning, followed by a period of slower drying rate.
From Figure 1 it can be observed that a drying constant rate period was not detected. We can assume that the drying occurred only in the falling rate period for all three investigated temperatures. The increased temperature determines decreasing of moisture content and the moisture ratio decreases proportionally with drying rate.
These results were in accordance with those of others authors that reported that drying rates increased with the increase in temperature and decreased in time for drying various vegetables such as pumpkin [11, 18] and red beetroot [19].

Effective moisture diffusivity and activation energy calculations

Effective moisture diffusivity values (Table 1) were calculated according to eqn. (3) described in the Materials and methods section.

Table 1. *Effective moisture diffusivity values of white button and brown mushrooms*

Sample	Temperature [°C]	R^2	$D_{eff} \cdot 10^{-10}$ [$m^2 \cdot s^{-1}$]
White button mushroom	50	0.9495	1.09665
	60	0.9832	1.47699
	70	0.9685	2.11723
Brown mushroom	50	0.9128	0.99522
	60	0.9550	1.53404
	70	0.9755	1.69885

Effective moisture diffusivity values increased directly proportional with drying temperature for both mushrooms species. The minimum value of effective moisture diffusivity was $0.99522 \cdot 10^{-10}$ $m^2 \cdot s^{-1}$ for brown mushroom at 50 °C, while the maximum value was $2.11723 \cdot 10^{-10}$ $m^2 \cdot s^{-1}$ for white mushrooms at 70 °C.
The R^2 (correlation coefficient, dimensionless) values were obtained by applying linear regression to the data in the slopes ln (*MR*) versus time plots.
The variation of ln (D_{eff})-[1/(T + 273.15] is presented in Figure 2 and the activation energy (*Ea*) values were calculated according equation 6.

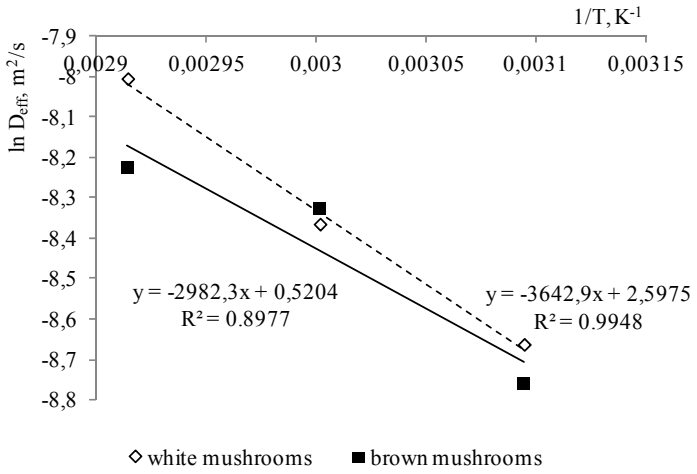

Figure 2. *Effective moisture diffusivity versus absolute temperature for white button and brown mushrooms*

Considering the literature reports, the activation energy values are from 12.7 to 110 $kJ \cdot mol^{-1}$ for food products [20].
In our study, for the tray drying of mushrooms, the activation energy for moisture diffusion, *Ea*, was calculated in range 24.79484 – 30.28707 $kJ \cdot mol^{-1}$, the higher value was for white mushrooms drying. These results indicate that white mushrooms need more energy input for tray drying process.

SEM analysis of tray dried mushrooms

During storage the white color and the compact texture of mushrooms underwent a rapid change, leading to deterioration in a relatively shorter period of time.
Scanning electron microscopy studies of white and brown mushrooms were made to show the microstructural changes during the drying treatments.
Figure 3 shows the cap tissue of the two mushroom types after tray drying at 50, 60 and 70 °C compare with the fresh one.
During the drying process, the intercellular spaces between hyphae cells of surface pilei tissue enlarged and became more pronounced when the temperature increased, especially for the brown mushrooms [21, 22].
The cavitation phenomenon is possible to be the result of the decreasing hyphae turgidity when the water is lost. It is known in the literature that the heat treatment applied induced the coagulation of the cell proteins and the disruption of the compartmentalizing intracellular membranes. So, the tissue loses its capacity to hold the water and became shrinks [22, 23].

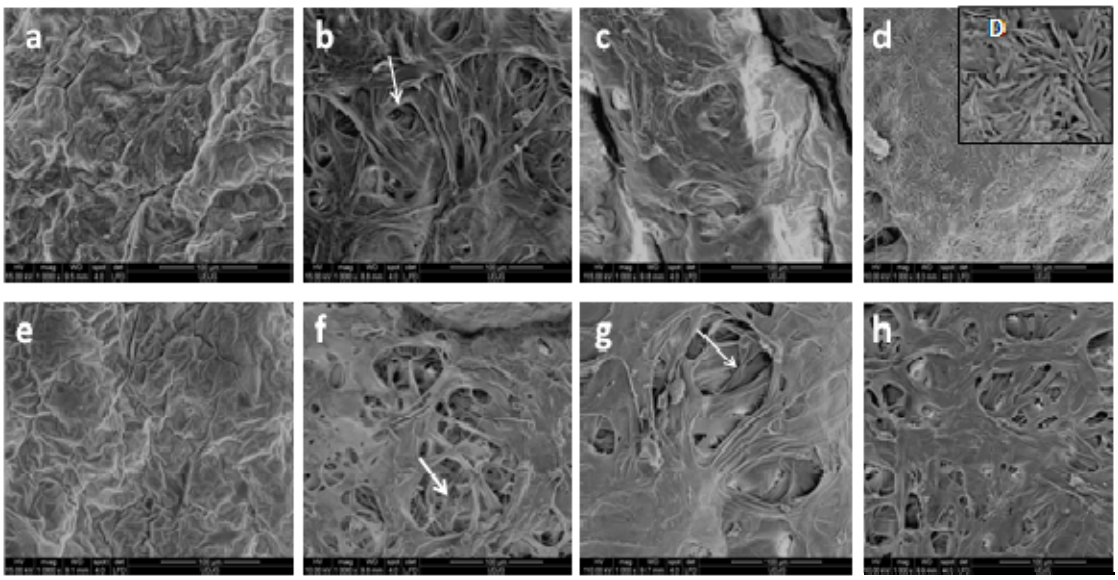

Figure 3. *SEM micrograph of cap white (a - d) and brown mushrooms (e - h); Fresh mushroom (a, e); Tray drying at 50 °C (b, f); 60 °C (c, g); 70 °C (d, h).*
(the arrows show the cavitation phenomena; Magnification, X 1000;
D – crystals of calcium oxalate (x 2000))

However, the loss of water during drying processes does not destroy the overall integrity of the tissue and some hyphae from the stipes of brown and white mushroom appeared intact and similar (Figure 4).

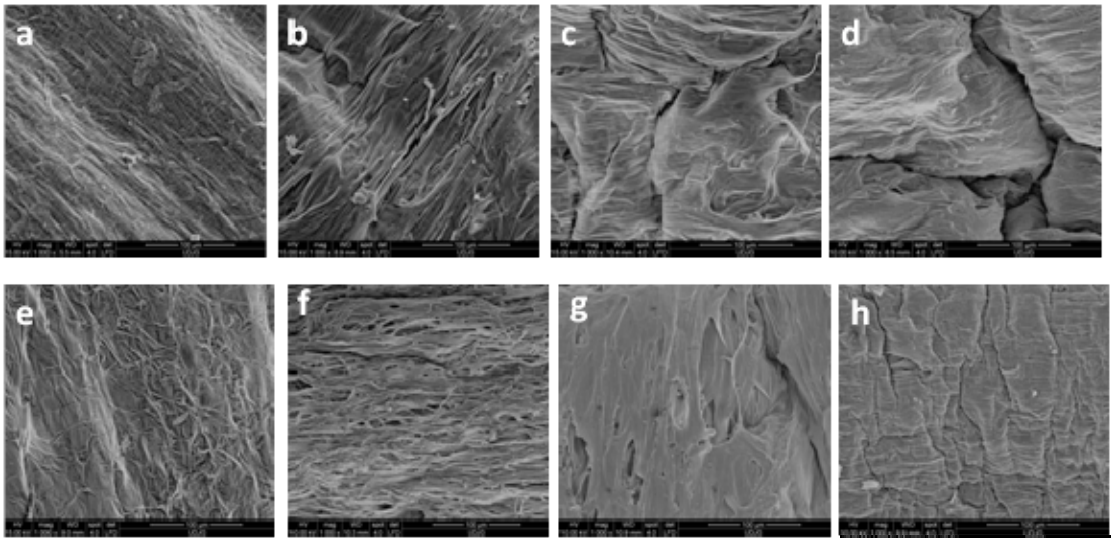

Figure 4. *SEM micrograph of stipes from white (a - d) and brown mushrooms (e - h); Fresh mushroom (a, e). Tray drying at 50 °C (b, f); 60 °C (c, g); 70 °C (d, h). Magnification, X 1000*

It is well known that chitin gives mechanical strength to the fungal cell wall [24]. In the drying process, both the space within the hyphae and their mechanical strength increases because of increased chitin level. So, when the mushrooms are subjected to the thermal treatment they look relatively firmness because of the higher mechanical strength.
An interesting observation is the presence of some hyphae with calcium oxalate crystals surrounding them. For the mushrooms dried at 70 °C, the presence of these crystals is more emphasize (Figure 3, d and D).
Oxalic acid represents a metabolite that results from the Krebs cycle and is often encountered in *Agaricus bisporus* [25, 26].
Calcium oxalate has a definite role in the hydrophobic cell coating and is located more or less tangentially on the hyphae surface [27]. Also, calcium oxalate is a common constituent of plant cells and was supposed to be involved in the plant defense process and in the carbon storage for later utilization under certain conditions [28]. Cellular tissue collapse and fiber structure modifications were observed by [16] after shiitake mushrooms convective air drying.

Color measurement

One of the most important sensorial attribute is color of food products. Table 2 presents the *L, a, b* and total color change *(ΔE*) for fresh and tray dried mushrooms at 50, 60 and 70 °C.
The color measurements indicated that the *L* values decreased with increased drying temperatures for both types of mushrooms, so the browning is more pronounced at higher temperatures. Also the total color change (*ΔE)* was greater in the samples dried at 70 °C.

Table 2. *L, a, b and total color change (ΔE) values for different tray drying temperatures*

Temperature [°C]	Color parameter	White button mushroom	Brown mushroom
Initial values	*L*	80.6	81.9
	a	4.3	1.18
	b	17.2	14.32
50	*L*	70.06	69.78
	a	2.49	2.54
	b	17.13	16.29
	ΔE	10.68	12.33
60	*L*	61.32	59.35
	a	2.62	3.21
	b	12.26	15.25
	ΔE	20.73	22.66
70	*L*	60.10	56.80
	a	3.15	2.98
	b	15.40	14.67
	ΔE	19.62	25.17

According to the [9] this implies that with increase in air temperature, the degradation rate of color becomes faster as a result of high energy transferred to the inside of food material. For fresh mushrooms typical *L* values for the caps and stipes were 80.6 for white button and with 1.61 % higher for brown strain mushrooms.

CONCLUSIONS

The convective air drying in a tray drier was applied for slices of mushrooms. The air temperature was an important factor that influenced the sensory attributes of mushrooms. The drying time decreased with temperature increase (2.17 h at 70 °C and 4.93 h at 50 °C to complete the drying process).

The activation energy for the brown mushrooms was lower than in white mushrooms. This means that more energy was needed to expel water from the white mushrooms system and a higher activation energy input was required.

The total color parameter (*ΔE*), the values of *L* and *a* were significantly ($p < 0.05$) influenced by the drying temperatures. The total color changes (*ΔE*) were higher, while the *L* values were lower in the brown mushrooms samples than in white mushrooms dried at all three temperatures.

SEM micrographs indicate the presence of some hyphae with calcium oxalate crystals surrounding them, especially for the mushrooms dried at 70 °C.

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