The influence of freeze drying conditions on microstructural changes of food products

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Abstract

The drying of food products can result in significant changes in the chemical composition, morphology and physical properties of foods and can lead to stabilized products with longer shelf-life and easier commercialization. Information on porous structure of foods is very important, characterizing the quality and texture of dehydrated food products. Therefore, structural properties, such as porosity, bulk density and true density of freeze-dried food products were investigated as affected by process conditions. Rice kernels were boiled for different time periods and agricultural products, including potato, mushroom and strawberry, were cut into cubes. The samples were frozen, tempered in liquid N\textsubscript{2} and freeze-dried, under various vacuum conditions, using a laboratory freeze-dryer. True density of the products was measured using a helium stereo-pycnometer. Bulk density was obtained by measuring the dimensions of the samples with a Vernier caliper. Simple mathematical models were developed in order to correlate the structural properties with process conditions. The microstructure of food products was also analyzed by Scanning Electron Microscopy and image analysis. Bulk density of freeze-dried materials increased with the applied pressure during freeze-drying, while porosity decreased. In addition, bulk density of freeze-dried rice kernels decreased with the increment of boiling time, while porosity increased. The changes in bulk density and porosity were closely supported by microstructural observations, according to SEM images. The microstructural changes of products, freeze-dried under various vacuum conditions, can be predicted using the proposed models and image analysis.

Keywords: agricultural products; freeze drying; rice; SEM; structure

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1. Introduction

Dehydration operations are widely used for the preservation of foods, since the removal of water minimizes the microbial spoilage and prevents the physical and chemical reactions of the foods’ compounds during storage [1, 2]. Dehydrated food products are easily obtained and maintain the characteristics of natural products [3]. Drying procedure comprises of simultaneous heat and mass transfer, which cause significant changes in the physical and chemical composition as well as in the structure of food products, depending on the transport mechanisms applied. Therefore, the microstructure and morphology of foods and as a result the quality of the final product, are related to the drying method and selected conditions applied [2].

Among the drying methods that are used in food processing industries, freeze-drying is considered one of the most advanced methods for drying high value products sensitive to heat, since it prevents undesirable shrinkage and produces materials with high porosity, unchanged nutrition quality, superior taste, aroma, flavor and color retention, as well as better rehydration properties [4], superior to those dried with conventional techniques.

Freeze-drying is used for the preservation of sensitive materials and the facilitation of transport and is carried out in two stages; the product is first frozen and then the ice is removed by sublimation directly from the solid to the vapor phase. During freeze-drying, ice sublimation causes significant changes in the shape and volume of the food products. Depending on the process conditions, the ice crystals which sublimate create pores or gaps with different characteristics, thus, it seems very interesting to investigate the effect of freeze-drying process conditions on the structural properties of food products [4].

Structural properties, like density and porosity, characterize the texture and quality of dehydrated products by controlling the taste and appearance. Besides the porosity of food products, pore size distribution plays a crucial role. Pore size distribution can be estimated by image analysis of two dimensional images [5]. Information on porous formation in foods during processing is needed for process design, influencing a wide variety of other properties, such as mechanical properties, thermal conductivity, thermal diffusivity and mass diffusion [2, 6].


The objective of the present research was to determine the effect of process conditions on the structural properties of freeze-dried food products. Freeze-drying was performed under controlled drying conditions, regulating pressure during drying. Simple mathematical models were developed according to the experimental data, in order to predict the values of porosity and bulk density correlated with process conditions. The microstructure of food products was also analyzed by Scanning Electron Microscopy and image analysis.

2. Materials & Methods

2.1. Freeze Drying

Parboiled rice and fresh agricultural products, including potato, mushroom and strawberry, were chosen as raw materials. The materials were stored at room temperature and dark conditions before the experimental procedure. Rice was boiled in excess de-ionized water at 100°C for different time periods, ranging from 4 to 24 min. Agricultural products were cut into cubes of approximately 20 mm length, 20 mm width and a thickness of 10 mm. The materials were then frozen at -30°C for 72 h, tempered for 1 h
in liquid N\textsubscript{2} and dehydrated for 24 h in a laboratory freeze-dryer (Leybold-Heraeus GT 2A). Freeze-drying was performed under various vacuum conditions, ranging from 0.04 to 1.25 mbar for rice samples and 0.06 to 1.50 mbar for agricultural products. The vacuum was reduced by leaking air through one of the pressure release valves. Two replicates for each drying condition were performed.

2.2. Measurement of bulk density, true density and porosity

The mass of the dried materials was measured using an electronic balance with an accuracy of 10\textsuperscript{-4} g. The true volume of the samples, ground to powder to remove most of the internal pores, was estimated using a stereopycnometer (Quantachrome multipycnometer MVP-1) with an accuracy of 0.001 cm\textsuperscript{3}, utilizing helium gas. Three replicates of each sample were used. The true density was expressed by the equation:

$$\rho_{ts} = \frac{m_s}{V_s}$$

(1)

where \(\rho_{ts}\) (g cm\textsuperscript{-3}) is the true density, \(m_s\) (g) the mass of dry solids and \(V_s\) (cm\textsuperscript{3}) the volume of dry solids.

The total (bulk) volume was obtained by measuring the actual geometric characteristics of freeze-dried materials, using a digital Vernier caliper with an accuracy of 0.001 cm. The results were the average of fifteen replicates for rice kernels and four replicates for agricultural products. Each rice kernel is considered to consist of a cylindrical part and two hemispheres. The total volume of rice kernels was estimated using the equation:

$$V_t = \frac{\pi \cdot d^2 \cdot (h - d)}{4} + \frac{4}{3} \cdot \pi \cdot \left(\frac{d}{2}\right)^3$$

(2)

where \(V_t\) (cm\textsuperscript{3}) is the total volume of each rice kernel, \(d\) (cm) the diameter and \(h\) (cm) the height of the cylindrical part of the rice kernel.

The total volume of freeze-dried cubes of agricultural products was estimated using the equation:

$$V_t = L \cdot W \cdot H$$

(3)

where \(V_t\) (cm\textsuperscript{3}) is the total volume of each dried sample, \(L\) (cm) the length, \(W\) (cm) the width and \(H\) (cm) the thickness of each sample.

The bulk density was determined using the equation:

$$\rho_{bs} = \frac{m_s}{V_t}$$

(4)

where \(\rho_{bs}\) (g cm\textsuperscript{-3}) is the bulk density and \(m_s\) (g) the mass of dry solids.

The porosity was estimated using the equation:

$$\varepsilon = 1 - \frac{\rho_{bs}}{\rho_{ts}}$$

(5)
2.3. Mathematical modeling

Several mathematical models were developed in order to predict the values of porosity and bulk density correlated with freeze-drying conditions for agricultural products and freeze-drying conditions and boiling time for rice kernels. The simplest and most appropriate power models were selected according to the Eq. (6) for rice kernels and Eq. (7) for agricultural products:

\[ \varepsilon = k_0 \cdot \left( \frac{P}{P_0} \right)^{m_0} \cdot \exp \left( \frac{t}{t_0} \right)^{n_0} \]  

(6)

\[ \varepsilon = k_1 \cdot \left( \frac{P}{P_0} \right)^{m_1} \]  

(7)

where \( k_0, k_1, m_0, m_1, n_0 \) are parameters dependent on the material, \( \varepsilon \) is the porosity, \( P \) (mbar) is the pressure in the freeze-dryer, \( t \) (min) is the boiling time, \( P_0 \) (mbar) and \( t_0 \) (min) are the corresponding values at reference conditions. Specifically, \( P_0 \) is the pressure at -20°C equal to 0.80 mbar and \( t_0 \) is the average value of boiling time equal to 14 min.

2.4. Scanning Electron Microscopy

Scanning Electron Microscopy (SEM) was used to visualize the microstructure of freeze-dried rice kernels and agricultural products. Freeze-dried materials were coated with gold using a SC7620 Mini Sputter Coater (Quorum Technologies). The specimens were then photographed using a Scanning Electron Microscope (Quanta 200 FEI (2004)) operated at 20 kV for rice kernels and 25kV for agricultural products for various magnifications.

2.5. Data Analysis

The obtained data from SEM images were processed with image analysis in order to estimate the pore size distribution. Regression analysis was used to estimate the models’ parameters. The influence of process conditions on the structural characteristics of freeze-dried food products was also analyzed using analysis of variance (ANOVA). The analyses were performed using Statistica software (Statistica Release 7, Statsoft Inc, Tulsa, OK, USA).

3. Results & Discussion

3.1. Bulk Density, True Density and Porosity

True density of freeze-dried food products was determined using Eq. 1 and it was considered constant, equal to the density of the solid material. The values of true density and the standard deviation, of each dried product are shown in Table 1.

<table>
<thead>
<tr>
<th>Material</th>
<th>Rice</th>
<th>Potato</th>
<th>Strawberry</th>
<th>Mushroom</th>
</tr>
</thead>
<tbody>
<tr>
<td>True density (g/cm³)</td>
<td>1.504±0.033</td>
<td>1.543±0.012</td>
<td>1.591±0.039</td>
<td>1.602±0.056</td>
</tr>
</tbody>
</table>

Bulk density of freeze-dried food products was found to be a strong function of freeze-drying conditions. As far as rice kernels are concerned, bulk density was significantly affected by boiling time. The corresponding results are presented in Figs. 1 and 2, for rice kernels and agricultural products.
respectively. Regression analysis showed that bulk density of freeze-dried materials decreased significantly \((p < 0.001)\) with the decrement of the applied pressure. In addition, rice kernels boiled for longer time period showed significantly \((p < 0.001)\) lower values of bulk density compared to those boiled for a short time period. Among the agricultural products, potatoes presented the highest bulk density, while mushrooms showed the lowest one.

![Fig. 1. Correlation of bulk density of freeze-dried rice kernels with boiling time, for various applied pressures during freeze-drying.](image1)

As it can be seen in Figs. 3 and 4, porosity of freeze-dried materials, measured using helium stereopycnometer, was significantly \((p < 0.001)\) influenced by freeze-drying conditions. At low pressures, porosity was the highest noticed and decreased as the pressure increased. Mushrooms presented more porous structure among the other agricultural products, whereas potatoes showed the lowest porosity.

![Fig. 2. Correlation of bulk density of freeze-dried agricultural products with applied pressure during freeze-drying.](image2)

![Fig. 3. Correlation of porosity of rice kernels, with boiling time for various applied pressures during freeze-drying.](image3)
In addition, porosity of freeze-dried rice kernels was significantly ($p < 0.001$) affected by boiling time, presenting higher values while elongating boiling procedure. Freeze-dried rice boiled for shorter time period showed the lowest values of porosity and the highest values of bulk density. As boiling time increases, there will be a higher water uptake reaching about 2.5 times the mass of dried rice. Therefore, a bulk volume increase will take place. During subsequent freezing and freeze-drying the ice sublimation creates pores. The amount of pores (porosity) is related to the water uptake and is higher when the water uptake is increased. Consequently, if no collapsing would happen due to the extension of boiling time, the porosity would be higher. The increase of porosity of rice kernels with increasing boiling time, varied from 40 to 50%, using as a reference the shortest boiling time, depending on the pressure applied.

![Graph showing correlation of porosity of freeze-dried agricultural products with applied pressure during freeze-drying.](image)

Fig. 4. Correlation of porosity of freeze-dried agricultural products with applied pressure during freeze-drying.

The results of parameter estimation of the mathematical model for porosity and bulk density of freeze-dried food products, measured using helium stereopycnometer, are summarized in Table 2.

<table>
<thead>
<tr>
<th>Material</th>
<th>$k_0$</th>
<th>$n_0$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rice</td>
<td>0.208±0.001</td>
<td>-0.017±0.002</td>
<td>0.988</td>
</tr>
<tr>
<td>Potato</td>
<td>0.876±0.001</td>
<td>-0.014±0.001</td>
<td>0.943</td>
</tr>
<tr>
<td>Strawberry</td>
<td>0.929±0.001</td>
<td>-0.014±0.001</td>
<td>0.951</td>
</tr>
<tr>
<td>Mushroom</td>
<td>0.947±0.001</td>
<td>-0.010±0.001</td>
<td>0.945</td>
</tr>
</tbody>
</table>

3.2. Scanning Electron Microscopy

The alterations of porosity of freeze-dried products as a function of boiling period and drying conditions are visualized with SEM images and presented in Figs. 5 and 6. Scanning Electron Microscope was operated at 100x magnification for strawberries and 500x magnification for the other food products. As it can be seen, the increase of boiling time leads to an increase in porosity and pore size of rice kernels. In addition, as far as freeze-drying pressure is concerned, when the absolute pressure in the freeze-drying chamber is higher, then the porosity is lower.
Fig. 5. Microstructure of freeze-dried rice as a function of boiling time and applied pressure during freeze-drying  a) \( P=0.04 \) mbar, \( t=4 \) min, b) \( P=0.04 \) mbar, \( t=20 \) min, c) \( P=1.25 \) mbar, \( t=4 \) min, d) \( P=1.25 \) mbar, \( t=20 \) min.

Fig. 6. Microstructure of freeze-dried agricultural products as a function of the applied pressure during freeze-drying a) Potato, \( P=0.06 \) mbar, b) Potato, \( P=1.00 \) mbar, c) Strawberry, \( P=0.06 \) mbar, d) Strawberry, \( P=1.00 \) mbar, e) Mushroom, \( P=0.06 \) mbar, f) Mushroom, \( P=1.00 \) mbar.

Fig. 7 presents the pore size distribution of freeze-dried products, estimated using image analysis. The percentage of large pores is higher at the lower applied pressure, where the porosity is higher.

Fig. 7. Pore size distribution of freeze-dried rice and potatoes as a function of the applied pressure during freeze-drying a) Rice, \( t=20 \) min, b) Potato.

4. Conclusion

Freeze-drying conditions significantly affected bulk density and porosity of dried food products. Boiling time also affected the structural properties of freeze-dried rice kernels. Bulk density decreased and porosity increased when decreasing the applied pressure during freeze-drying. In addition, rice samples boiled for lower time period presented the lowest value of porosity and the highest value of bulk density, while those boiled for higher time period showed the highest value of porosity and the lowest
value of bulk density, respectively. The above results were visualized with Scanning Electron Microscopy and image analysis.

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References


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