HEAT PUMP FLUIDIZED BED DRYING OF COD FISH

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ABSTRACT

Several cod fish drying trials were performed using a heat pump fluidized bed dryer. Norwegian commercial frozen cod fish was granulated, screened and stored at freezing temperatures (-20 °C) in order to maintain its original characteristics prior to processing. The tests were done using two different bed volumes and drying temperatures below (-10 and -5 °C) and above (0, 15, 30 °C) freezing point and also their combination (-10/30 °C and -5/30 °C) to study possible effects on drying kinetics, quality and properties. The moisture content, water activity and color were determined during drying process by taking samples at pre-established time intervals. Also rehydration ability and bulk density of the dry sample were measured. Drying kinetics were modeled using diffusion and empirical models, from which the activation energy was estimated. Bed volume affected drying rate but had no influence on product properties. Drying rate increased with temperature and the product properties changed according drying temperature. The product dried at atmospheric freeze drying conditions (-5 and -10 °C) had lower bulk density, higher brightness and rehydration ability when compared with samples dried at positive temperatures (15 and 30 °C). The runs dried at 0 °C showed intermediate values for these characteristics. The combination of temperatures decreased drying time and had no influence on the product final properties.

INTRODUCTION

With the awareness on the issues concerned to quality, environmental and energy utilization the society expresses desire for better products and for more efficient and environmentally friendly processes. Therefore, R&D addressing such topics is technically important and socially necessary. The preservation
and storage of foodstuffs require drying (Alves-Filho and Strommen, 1996). During drying moisture content is reduced until a safe level in which there is a minimum spoilage caused by microorganisms, enzymes and other agents.

When properly designed the heat pump is among the most efficient way to supply heating and cooling as required in drying. Heat pump dryers have the features to process heat sensitive foodstuffs due to the wide temperature range in which operate (-20 to 100 °C). Heat and mass transfer is increased in a low temperature heat pump dryer by using fluidized bed mode which promotes better contact between suspended particles and air. Heat pump fluidized bed drying at temperatures lower than freezing point is known as atmospheric freeze drying.

The cod fish is a source of protein with low fat content. Fishing period in Norway is concentrated in a relatively short time period from December to April. Then, drying would be a logistic alternative to supply dried fish around year by lowering the moisture and water activity of the raw material. Usually, atmospheric freeze drying of fish minimizes fatty acid oxidation and reduces protein denaturation (Alves-Filho, 2004).

The main objective of this work is to determine the effects of heat pump fluidized bed drying conditions on cod fish properties in a wide range of temperatures (-10 and 30 °C). Measurements were done by sampling and analysis of relevant quality and properties.

MATERIALS AND METHODS

Raw material and sample preparation

The raw material for the experiments was frozen Norwegian cod fish that was pressed and frozen in form of slabs (mass 100 g, dimensions: 6.3 cm width, 7.5 cm long and 2 cm thick). The slabs were maintained frozen (-20 °C) until being granulated in particles of random size but with a thickness between 2 and 3 mm. The sample preparation was made in a freezing-room at -20 °C temperature to avoid melting and to facilitate granulation.

Heat pump fluidized bed dryer

The heat pump fluidized bed dryer used in the experiments is depicted in the Figure 1. The dryer had a drying chamber and blower and the heat pump main components were the compressor, evaporator, condensers and valves. The drying air is recirculated in order to enhance the energetic efficiency of the process. Thus the drying chamber outlet air is dehumidified and cooled in evaporator and heated in the condenser to reach the desired drying chamber inlet air temperature. The air temperature is controlled by the heat pump three-way valve by redirecting refrigerant flow either into condenser 1 or 2. The cylindrical drying chamber was made of methacrylate with a 0.25 m diameter and a 0.5 m height. All the drying circuit in contact with the surroundings was thermally insulated.

The different process variables were logged using a data acquisition unit (Fluke hydra) continuous recording, monitoring and display of inlet air velocity (m/s), relative humidity (%) and temperature (°C). Also the outlet air temperature and relative humidity were recorded.
Drying conditions

Drying experiments were carried out at freeze drying conditions (-10 and -5 °C) and low or medium air drying temperatures (0, 15 and 30 °C) and also combination (-10/30 and -5/30 °C). The air velocity was kept between 1.5 and 2.5 m/s using a frequency inverter (Hitachi, HFC-VWS) and controlled to maintain fluidization.

Two different raw material loads were used in the experiments: 3.30 g cm\(^{-2}\) which correspond to a bed volume of 4 L and 1.65 g cm\(^{-2}\) for a bed volume of 2L. The initial bulk density of the bed was 375 g/L.

Table 1 shows the experimental design carried out in this work based on inlet air temperature and drying chamber bed volume.

<table>
<thead>
<tr>
<th></th>
<th>-10</th>
<th>-5</th>
<th>0</th>
<th>15</th>
<th>30</th>
<th>-5/30</th>
<th>-10/30</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>2L</strong></td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td><strong>4L</strong></td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1. Experiments carried out at different temperatures (°C) and bed volume (L)

Experimental measurements

Drying kinetics were determined taking samples at regular period of times and measuring moisture content using an infrared moisture meter (Precisa HA300). Water activity and color of the samples were also determined during and after the drying experiments. Water activity was measured using the Aqualab meter (model CX-2) at room temperature 25±2 °C and the color was determined using an X-Rite 948 spectrophotometer (with CIE 1964 10° observer and illuminant D\(_{65}\)). The results were expressed in CIELAB space coordinates (L, a and b).

The bulk density of the bed was measured before and after drying using a standard mass-volume method. Finally the rehydration ability was assessed by placing the samples in tap water at room temperature (18±2 °C) during 6 min and measuring the initial and final weight of the samples. Rehydration ability was calculated as the ratio between final and initial sample weight using averaged values from triplicate samples.
**Modeling drying kinetics**

A diffusion model for a slab, expressed by Equation 1, was used for the mathematical description of the drying kinetics. The model assumes the initial moisture content uniformly distributed throughout the solid, non-shrinkage and solid surface at equilibrium with drying air (Simal et al., 1998).

\[
W(t) = W_e + (W_c - W_e) \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \exp \left( -\frac{D_e (2n+1)^2 \pi^2 t}{4L^2} \right)
\]  

(1)

It is important to compare the results of drying kinetics obtained from empirical and theoretical models. For that purpose the proposed expression is given by the Weibull model (Cunha et al., 2001):

\[
W(t) = W_e + (W_c - W_e) \cdot \exp \left( -\frac{t}{\beta} \right)^{\alpha}
\]  

(2)

The effective mass diffusivity and the kinetic parameters of the empirical models follows the Arrhenius equation that includes the drying air temperature (Sanjuán et al., 2004; Mulet et al., in press) and the activation energy according to the expressions:

\[
D_e = D_o \exp \left( \frac{-E_a}{R_g (T + 273)} \right)
\]  

(3)

\[
\frac{1}{\beta} = \frac{1}{\beta_0} \exp \left( \frac{-E_a}{R_g (T + 273)} \right)
\]  

(4)

**Modeling desorption isotherm**

The GAB model was used to describe the relationship between water activity and moisture content measured at room-ambient conditions (25±2 °C) (Mulet et al., 2002).

\[
W = W_m \frac{C K a_w}{(1 - K a_w)(1 + (C - 1) K a_w)}
\]  

(5)

**Parameters identification**

The software known as Solver (Microsoft Excel XP™) was used to determine the parameters of the models, \(D_e\) in diffusion model and \(\alpha\) and \(\beta\) in Weibull model. Due to the difficulty in reliable measurement the half thickness of the granulated samples (L), the parameter \(D_e\) in the in diffusion model was combined to L to form a single parameter (\(D_e/L^2\)). Solver is a non linear optimization method that uses the generalized reduced gradient method to reach the optimum value. The objective function selected to be minimized consisted on the sum of the squared differences between experimental and calculated average moisture contents. The closeness of the fit was assessed by computing the variance of the models (Mulet et al., in press).

\[
VAR = \left( 1 - \frac{S_{yx}^2}{S_y^2} \right)
\]  

(6)

The parameters of GAB model (C, K and \(W_m\)) were also determined using Solver and similar procedure as above mentioned.
RESULTS AND DISCUSSION

Water activity and moisture content relationship \((W/aw)\)

Figure 2 shows the plot of moisture content versus water activity for the cod fish samples dried at different experimental conditions. The data points overlap, which indicate similar effect by the different experimental conditions. Therefore, all the experimental data points were modeled together with a single GAB model.

The parameters identified with GAB model were \(W_m = 0.051 \text{ kg kg}^{-1}\), \(C = 1.262\) and \(K = 0.922\) and the correlation was satisfactorily good (VAR 0.993). Sablani et al. (2001) obtained similar value of the monolayer moisture content \((0.049 \text{ kg kg}^{-1})\) for desorption isotherms of freeze dried fish sardines determined at 25, 40 and 50 °C.

Temperature effect on drying rate

Drying kinetics of cod fish done at constant temperature and with bed volume of 2L are plotted in Figure 3. The falling rate period seems to be the predominant element in the drying kinetics of cod fish, and this allows taking the initial moisture content as critical moisture content.

Drying kinetics of cod fish follows the usual behavior of foodstuffs and the drying rate increases with the rise of the air inlet temperature. Based on the experimental data the diffusion and empirical models were used to describe the drying kinetics. The models’ parameters and variance were determined as given in Table 2. The diffusion model presented lower values of VAR than the Weibull model. A probable cause for this is that assumptions made for the diffusion model, such as non-shrinkage and constant effective mass diffusivity, are unsuitable to describe cod fish drying. Mittal (1999) reviewed mass diffusivity data for different foodstuffs such as drying frozen fish flesh at -5, -10, -15, -20 and -25 °C, and reports \(D_e\) around \(10^{-12} \text{ m}^2 \text{ s}^{-1}\). Consistently, the samples with thickness of 2-3 mm had effective mass diffusivity similar to that value.
Figure 3. Drying kinetics of cod fish at different temperatures (°C) and bed volume of 2L.

Table 2. Modeling drying kinetics of cod fish determined at different temperature (°C), bed volume 2L.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>Diffusion model</th>
<th>Weibull model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(D_e/L^2 \times 10^{-5} \text{ s}^{-1})</td>
<td>(\alpha)</td>
</tr>
<tr>
<td>-10</td>
<td>1.10</td>
<td>0.941</td>
</tr>
<tr>
<td>-5</td>
<td>1.56</td>
<td>0.931</td>
</tr>
<tr>
<td>0</td>
<td>2.92</td>
<td>0.914</td>
</tr>
<tr>
<td>15</td>
<td>4.70</td>
<td>0.913</td>
</tr>
<tr>
<td>30</td>
<td>6.55</td>
<td>0.946</td>
</tr>
</tbody>
</table>

Activation energy was calculated from the plot of \(\ln \frac{D_e}{L^2}\) and \(\ln \frac{1}{\beta}\) against \(1/T\) as shown in Figure 4. The data obtained for higher temperature (15 and 30 °C) departs from the linearity trend of data for samples dried at lower temperatures (-10, -5 and 0 °C). Thus, a single linear relationship can not describe these two different processes together. Also, temperature difference implies different states of the water fraction present in the samples, which can be liquid, ice or partially frozen. The additional difference is in the structures of products due to drying at different temperatures.

Activation energy may be calculated using either the data obtained at high (0, 15 and 30 °C) or low temperatures (-10, -5 and 0°C). Even though only three points were used in each determination, approximated activation energy may be estimated for each of the models. Using data at higher temperatures the activation energies estimated were 18.6 and 19.5 kJ mol\(^{-1}\) for the diffusion and Weibull models. These values are lower than those obtained at lower temperatures, which were estimated as 58.2 and 54.7kJ mol\(^{-1}\) for the diffusion and Weibull models. Obviously, the energy required to dry the cod fish at low temperatures is larger than at high temperatures.
Diffusion model

Weibull Model

Figure 4. Plot of $\ln \frac{D_e}{L^2}$ and $\ln \beta$ against $1/T$ for activation energy identification.

Figure 5 shows the effect of the combination temperatures in drying of cod fish for experiments performed with bed volume of 4 L. The low temperatures of -5 and -10 ºC are used as first steps of the drying and positive temperature of 30 ºC is used to finalize and speed-up drying.

Figure 5. Effect of the combination of drying temperatures (ºC), bed volume 4L.

The combination of temperatures increases drying rate or reduces residence time. The final drying temperature also affects the equilibrium moisture content, which drops for higher air inlet temperatures or lower relative humidities.
Effect of bed volume on drying rate

The drying kinetics tests carried out at -5 and -10 °C with bed volumes of 2 and 4 L are plotted in Figure 6.

The increase of the bed volume required longer drying time for the same experimental conditions. As expected, a higher sample volume leads to higher bed height. The air humidifies as it flows through the bed and it picks more moisture. Then, higher bed leads to reduce drying capacity and extends drying time.

Effect of drying temperature and bed volume on quality properties of cod fish

The effect of drying experimental conditions on rehydration ability of dry cod samples is shown in Figure 7A. This property was affected by drying temperature, samples dried at freezing temperatures showed higher rehydration ability than samples dried at high temperature (15 and 30 °C), while samples dried at 0°C had intermediate values. Higher temperature drying leads to intense shrinkage and a decrease in rehydration ability (Mayor and Sereno, 2004). The sample’s bulk density is also affected by shrinkage which causes reduction in volume and increase in the bulk density, as shown in Figure 7B. However, the bed volume had no observable effect on rehydration ability and bulk density.

CIELAB coordinate L is associated with the brightness of samples and an increase of this value implies higher brightness. Figure 7B shows the evolution of parameter L of cod fish samples during drying at -10, 0 and 30°C for a bed volume of 2L. Brightness increased as moisture content drops until a level close to 30%wb, from which the brightness remained constant (Figure 7D). The average of brightness for samples dried at several conditions and with moisture content below 30%wb is presented in Figure 7C. It indicates that the brightness of samples was influenced by drying temperature and samples dried at freezing temperatures had higher brightness than runs dried at 15 and 30°C. Similarly to rehydration ability and bulk density, the samples dried at 0 °C had intermediate color. As in the rest of properties, bed volume had no effect on samples color either. Additionally, a and b color components were less affected by drying temperature.
Figure 7. Effect of drying temperature and bed volume on dry cod fish quality. A: rehydration ability, B: bulk density, C: brightness of dry samples with moisture content lower than 30 % wb and D: evolution of brightness with moisture content during drying, bed volume of 2L.

CONCLUSIONS

Drying kinetics of cod fish were carried out at different experimental conditions in a heat pump fluidized bed dryer. Drying temperature tested were -10, -5, 0, 15 and 30 ºC, also temperature combination were used (-10/30 and -5/30), two different samples bed volumes in drying chamber were tested (2L, 4L).

As drying temperature was risen drying rate increased. The modeling of drying data concluded than drying kinetics carried out at temperatures lower than freezing temperature are not comparable to those performed at higher temperatures, since different process and product are involved.

Different quality properties of dry samples were measured (color, bulk density and rehydration ability). Compared with samples dried at high temperature the runs dried at freezing temperature had better quality and properties such as lower bulk density, higher rehydration ability and brightness. Consistently, the samples dried at 0 ºC had intermediate values of property and quality.

Fluidized bed volume affected drying rate but had no effect on product quality or properties.

ACKNOWLEDGEMENTS

Marie Curie Training Site Program (EU Commission) and Project AGL2001-2774-CO5-01.
LITERATURE


NOTATION

\( a_w \) Water activity

\( C, K \) Parameters GAB model

\( D_m \) Dry matter

\( D_e \) Effective moisture diffusivity \( m^2 \text{s}^{-1} \)

\( D_o \) Preexponential factor \( m^2 \text{s}^{-1} \)

\( L \) Half thickness \( M \)

\( R_g \) Universal gas constant \( \text{kJ mol}^{-1} \text{K}^{-1} \)

\( S_y \) Standard deviation of the sample

\( S_{yx} \) Standard deviation of the estimation

\( T \) Time \( S \)

\( T \) Air drying temperature \( ^\circ \text{C} \)

\( \text{VAR} \) Explained variance

\( W \) Average moisture content \( \text{kg of water} \text{100 kg total}^{-1} \text{ or } \%w_b \)

\( W_m \) Monolayer average moisture content \( \text{kg water} \text{kg dm}^{-1} \)

Greek symbols

\( \alpha \) Shape parameter

\( \beta \) Kinetic parameter \( s \)

\( \beta_0 \) Preexponential factor

Subscripts

\( E \) Equilibrium

\( C \) Critical