Drying kinetics of salted cod in a heat pump dryer as influenced by different salting procedures

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Abstract

In this study, the influence of different salting procedures on the drying kinetics of salted cod in a heat pump dryer was investigated and the changes in moisture ratio and drying rate were determined. The effect of phosphates and protein treatments on the colour, behaviour and distribution of water throughout the salted cod samples were measured. The results showed that there was no constant drying period; but two falling drying periods were observed. The drying rate at the first falling period was affected by phosphates treatment. However, this effect was not observed in the second falling period. The water mobility was affected by phosphates. The colour of the fish fillets was not affected by both phosphates and protein treatments.

Keywords: Gadhus morhua, phosphate, protein treatment, NMR, Vietnam, Iceland.

Introduction

Salted cod (Gadhus morhua) is one of the most important processed products for the economy of Iceland and constitutes 15-20% of the total value of seafood exports [1]. The traditional markets for Icelandic salted cod have been Portugal, Spain, Italy, Greece and Latin America [2, 3]. Salted cod is produced either by dry, brine, or injection salting or a combination of these methods. Regular salted cod reaches a salt concentration of 20-22% (w/w) and water content of 55-60% (w/w) [4]. The water content can be further reduced by drying and the obtained dried salted cod has water content of less than 50% (w/w) [5].
Drying is one of the thermal treatments applied in many food industries and the use of dried foods is expanding rapidly [6]. The goals of drying process research in the food industry are three-fold: economic considerations, environmental concerns and product quality aspects [7]. In many agricultural countries, large quantities of food products are dried to improve shelf-life, reduce packaging costs, lower shipping weight, enhance appearance, encapsulate original flavour and maintain nutritional value [8]. The drive towards improved drying technologies is promoted by the needs to produce better quality products. On the other hand, in most industrialised countries, the energy used in drying accounts for 7-15% of the total industrial energy used, often with a relatively low thermal efficiency ranging from 25% to 50% [8]. Some highly industrialised countries use over one third of their prime energy for drying operations. Consequently, in order to reduce the energy consumption, it is necessary to select an efficient heating system. The heat pump presents an efficient and environmentally friendly technology due to its low energy consumption [9] and the high coefficient of performance of the heat pump and the high thermal efficiency of a properly designed dryer [10]. In addition, heat pump drying can operate independently of outside ambient weather conditions [11].

Heat pump drying has the potential to operate more efficiently and at lower temperatures than conventional drying [12]. In heat pump drying, both sensible and latent heat can be recovered from the dryer exhaust humid air, improving the overall thermal performance. Heat pump drying can be operated over a wide range of temperatures, providing good conditions for drying of heat sensitive materials [13]. It can also improve the quality of food products due to its low drying temperature and independency of outdoor air. In recent years, interest in applying heat pump drying to food and biomaterials has been growing to enhance the quality of the final products [8]. Usually, dried products have a low aroma volatile content, suffer loss of heat-labile vitamins and have a high incidence of colour degradation [14]. Although, heat pump drying has been used extensively in industry for many years, application of heat pumps to dry fish and fish products is still limited and there is a lack of heat pump dryer characteristics data [15].

The aim of this present study was to investigate the influence of different types of salted cod on drying kinetics during drying in a heat pump dryer.

Materials and Methods

Production of salted cod fillets

Salted cod fillets (*Gadus morhua*) were processed by four different procedures in Visir hf., Djupivogur, Iceland, following a three-step salting process which included consecutive salt injection, brine- and dry-salting. Cod fillets were injected with four different brine solutions by an automatic multi-needle injector machine (Droit INJECT-O-MAT, PMS-42F-30I, Auburn NSW, Australia).

**Group A:** Cod fillets were injected with a brine concentration of 25%.

**Group B:** Cod fillets were injected with a mixture of 22.5% brine and 2.5% of phosphates (Carnal 2110, CFB Budenheim, Budenheim, Germany).

**Group C:** Cod fillets were injected with a mixture of 22.5% brine and 2.5% of protein.

**Group D:** Cod fillets were injected with a mixture of 20% brine, 2.5% protein and 2.5% of phosphates (Carnal 2110, CFB Budenheim, Budenheim, Germany).
The injected fillets of the four groups (A, B, C and D) were brined by immersing in brine concentration of 18% (w/w) NaCl for 2 days. Finally, injected brined cod fillets were dry salted in big plastic containers with outlet for brine for 14 days at 4°C ± 1°C. After this time period the fillets were packaged with excess salt in 25 kg waxed cartons and transported to the Matis Laboratory where the experiments were carried out.

**Drying process and sampling**

Ten fillets of each group were individually weighed and dried in a heat pump dryer for five days. After every day of the drying process, the samples were taken out to weigh in order to calculate the water loss and drying kinetics. The samples before and after drying were measured the colour, behaviour and distribution of water throughout. The drying temperature was controlled and fixed at 19°C, air velocity at 2.0 m/s and relative humidity at 60%.

**Drying kinetics**

The moisture ratio (MR) was calculated by Eq. (1) [16]:

$$MR = \frac{(W - W_e)/(W_o - W_e)}$$

Where MR was moisture ratio; W, W_e and W_o were moisture content at any drying time, equilibrium moisture content and initial moisture content of sample in dry matter, respectively.

The drying rate of the salted cod was obtained from Eq. (2) [17]:

$$\text{Drying rate} = \frac{(W_{t+dt} - W_t)/dt}$$

Where W_{t+dt} and W_t were moisture content at drying time (t + dt) (kg/kg dry matter) and moisture content at drying time (t) (kg/kg dry matter), respectively.

Second Fick’s law was used to calculate the effective moisture diffusivity (D_{eff}) during drying by Eq. (3) [18]:

$$MR = \sum_{n=1}^{\infty} \frac{1}{n\pi} \exp \left( -\frac{n^2 \pi^2 D_{eff} t}{L^2} \right)$$

Where D_{eff} was the effective moisture diffusivity (m²/s), L was the thickness of fish fillet (≅ 1.8 cm) and n was the number of terms taken into consideration (n = 1, 2, 3,...). When the drying time was long, the number of terms was set as n = 1. Therefore, the effective moisture diffusivity was calculated by using Eq. (4) [19]:

$$\ln(MR) = \ln \left( \frac{W - W_e}{W_o - W_e} \right) = \ln \left( \frac{6}{\pi^2} \right) - \frac{\pi^2 D_{eff} t}{L^2}$$

**Colour measurement**

The intensity of the flesh colour was measured by using the Minolta CR-300 chromameter (Minolta Camera Co., Ltd; Osaka, Japan) in Lab* system with CIE IlluminantC. The instrument records the L* (lightness), a* (redness) and b* (yellowness) values on CIELAB colour scale. The a* value describes the intensity in green colour (negative) and in red colour (positive). The b* value describes intensity in blue colour (negative) and in yellow colour (positive).
The metric chroma (C*) and colour difference (ΔE_H) values were calculated by using Eq. (5)-(6):

\[
C^* = \left[ (a^*)^2 + (b^*)^2 \right]^{1/2} \tag{5}
\]

\[
\Delta E_H = \left[ (\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2 \right]^{1/2} \tag{6}
\]

Nuclear Magnetic Resonance (NMR)

The behaviour and distribution of water throughout the salted cod samples was determined with Low Field Nuclear Magnetic Resonance (LF-NMR). A low-field Bruker Minispec mq 20, bench top NMR-analyzer (Bruker Optics GmbH, Am Silberstreifen D-76287 Rheinstetten, Germany), with test tubes of 10 mm width, were used for the measurements. All measurements were performed at STP using a Receiver Gain of 70 dB and a Recycle Delay of 10 s. The transverse relaxation time, T2, was measured with a Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence with an interpulse spacing of 250 µs, 16 scans and 8100 fitted points. The longitudinal relaxation time, T1, was measured with an Inversion Recovery (IR) pulse sequence with 30 measuring points, 4 scans and a duration factor of 1.322.

Water content

Water content was determined as weight loss after drying according to ISO 6496 [20].

Statistical analysis

Microsoft Excel 2007 (Microsoft Corp., San Leandro, Calif., U.S.A.) was used to calculate the means and standard deviations for all multiple measurements and to generate graphs. The data sets obtained were compared by multiple comparisons ANOVA by using all pair wise comparison by SigmaStat 3.5 (Jandel Scientific Software, Ontario, Canada). Significance of difference was defined at p<0.05.

Results and Discussion

Drying kinetic parameters

Generally, the moisture ratio and the drying rate of the salted cod in all groups decreased with increasing drying time (Figures 1a and b, respectively). No significant (p>0.05) differences in moisture ratio were found between the groups (Figure 1a). Nevertheless, during the first two days of drying, the samples with phosphates injection (group B) had a slightly lower drying rate compared to other groups (Figure 1b). This can be explained by the phosphate injection decreasing the water mobility, resulting in a lower drying rate. The results are in accordance with the results of NMR measurements, indicating that longer relaxation times were observed in the samples with phosphate treatments. In addition, the drying rates of all samples decreased rapidly at early stages of the drying process. This may be due to the surface of fish being initially wet and a continuous film of water existing on the drying surface. This water is removed easily, leading to a higher drying rate. With drying time, the drying rate decreased slowly. This may be attributed to water movement to the surface of the fish fillets accompanied by salt migration [21]. The rate of water evaporation on the surface is higher than the rate of water diffusion from the inner layers to the surface, resulting in formation of a crust which inhibits water evaporation [21, 22]. During the last three days of drying, the drying rates of all samples were similar and varied much, indicating that the water loss in this period was bound water with higher removed energy needed. The results also show that no constant drying rates were observed in all samples; therefore, the falling drying rate occurred directly. It may be due to high salt concentration in the fish muscle which does not leave any free water [22]. The results are in agreement with previous publications in drying African salted catfish, salted sardine and salted mackerel [21, 22, 23]. On the other hand, protein injection did not show any effects on moisture ratio and drying rate during drying.
The effective moisture diffusivity values of salted cod during heat pump drying are shown in Table 1. These results are in accordance with the results of moisture ratio and drying rate during drying. The $D_{\text{eff}}$ value of salted cod lacking phosphates and protein treatments (group A) was slightly higher than that of other groups (B, C and D). The $D_{\text{eff}}$ values obtained in this study were in the range of $10^{-11}$ to $10^{-9}$ m/s² that have been published for foodstuffs [24].

Table 1. Effective moisture diffusivity ($D_{\text{eff}}$) of salted cod during heat pump drying.

<table>
<thead>
<tr>
<th>Group</th>
<th>$D_{\text{eff}}$ (m²/s) ($\times 10^{-10}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>4.306</td>
</tr>
<tr>
<td>B</td>
<td>3.154</td>
</tr>
<tr>
<td>C</td>
<td>3.371</td>
</tr>
<tr>
<td>D</td>
<td>3.425</td>
</tr>
</tbody>
</table>

**Colour measurements**

The changes in $L^*$, $a^*$, $b^*$, $C^*$ and $\Delta E_H$ values of all samples during heat pump drying are depicted in Table 2. The lightness ($L^*$ values), red colour intensity ($a^*$ values) and yellow colour intensity ($b^*$ values) of all samples in all groups increased significantly ($p < 0.05$) after drying. However, no significant ($p > 0.05$) differences were found in $L^*$, $a^*$, $b^*$ values between the groups, indicating that phosphates and protein injection during the salting process did not affect the colour. The increase in lightness could be caused by the water removal during drying and formation of salt crystals in the fish muscle. The increase in red and yellow colour intensity may be due to the oxidation of pigment in the fish muscle by oxygen and enzyme oxidation [25].

The colour difference values were observed from 21.14 to 25.95 and no differences were found between the groups.
Table 2. Changes in colour parameters of salted cod during heat pump drying.

<table>
<thead>
<tr>
<th>Group</th>
<th>L*</th>
<th>a*</th>
<th>b*</th>
<th>C*</th>
<th>∆EH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BD</td>
<td>AD</td>
<td>BD</td>
<td>AD</td>
<td>BD</td>
</tr>
<tr>
<td>A</td>
<td>52.48</td>
<td>73.00</td>
<td>-2.65</td>
<td>-0.86</td>
<td>-3.64</td>
</tr>
<tr>
<td>B</td>
<td>50.44</td>
<td>75.01</td>
<td>-2.61</td>
<td>-0.93</td>
<td>-6.53</td>
</tr>
<tr>
<td>C</td>
<td>51.07</td>
<td>75.83</td>
<td>-2.50</td>
<td>-1.02</td>
<td>-4.89</td>
</tr>
<tr>
<td>D</td>
<td>54.06</td>
<td>74.80</td>
<td>-2.99</td>
<td>-1.05</td>
<td>-5.40</td>
</tr>
</tbody>
</table>

Note: “BD” before drying; “AD” after drying

NMR measurements

Relaxation times and apparent relative water population measurements of salted cod before and after drying are shown in Figure 2. The figure shows a significant (p<0.05) decrease in longitudinal (T₁) relaxation times (Figure 2a) and both transversal (T₂₁ and T₂₂) relaxation times (Figure 2b and c, respectively) in all groups during the drying. This was simply correlated to the water loss during the drying process, resulting in a lower relaxation time. In addition, longer relaxation times were observed in the phosphate treated groups (B and D) than the phosphate lacking groups (A and C), indicating that the addition of phosphate resulted in a decrease in water mobility in the samples. This is in correlation with the water holding capacity results, which state a significantly higher water holding capacity in the phosphate groups [26].

Figure 2d indicates on the other hand a large change in the apparent relative water population (A₁) of tightly bound water during the drying. Before the drying 60-66% of the water in the sample was tightly bound to the muscular structure, but after the drying this ratio went up to 85-89%, indicating that the freely moving water was removed more easily in the drying process, while more energy was needed to remove the tightly bound water. Before drying, it could be seen that the phosphate groups (B and D) had less tightly bound water than the phosphate free groups (A and C). This indicated that water was drawn out of the cells due to the phosphate addition and into the intracellular space. Nevertheless, no differences were found in A₁ values among the groups after drying. The results are in correlation with drying rate during the late stage of the drying process. Moreover, the protein addition did not affect both relaxation time and apparent relative water population of tightly bound water in the samples before and after drying.
Conclusion

The results of the present study indicate that the drying kinetics were affected by different salting procedures, however no significant influence was found. The phosphates showed an effect on decreasing the water mobility in the samples, resulting in a higher relaxation times and a lower drying rate. Inversely, protein injection did on other hand not affect both water mobility and drying rate. In addition, both protein and phosphate treatments did not affect the colour of fish before and after heat pump drying.

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References


