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Effect of temperature on nitrite and water diffusion in pork meat

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ABSTRACT

Nitrites are important food additives. The nitrite movement in meat is assumed to occur by means of a diffusion process. The objective of this study was to investigate the effect of temperature on nitrite and water diffusion mechanisms in meat samples during the curing of pork meat. For this purpose, cylinders of *Semimembranosus* muscle were salted with sodium nitrite ($NaNO_2$) at 2 °C, 7 °C and 12 °C. Experimental curing and water loss kinetics were modelled by means of a diffusion model. As the curing time lengthened, the water content fell and the nitrite content increased. The values for the nitrite and water diffusion were estimated to be in the range of $4.58 \cdot 10^{-12}$–$1.02 \cdot 10^{-12}$ m^2/s and $5.96 \cdot 10^{-9}$–$9.82 \cdot 10^{-9}$ m^2/s respectively, and they increased as the temperature went up. The activation energy was 32.24 kJ/mol for water diffusion and 60.32 kJ/mol for nitrite diffusion.

1. Introduction

Meat products are preserved by means of different methods, salting and curing being one of the most commonly used. Sodium chloride (NaCl) is an ingredient which, among other things, enhances the flavour and decreases the water activity of the product. Nitrite is an additive giving the cured products their characteristic red colour and flavour (Flores and Toldrá, 1993). Nitrite, together with sodium chloride, inhibits the production of the neurotoxin produced by *Clostridium botulinum*, thus preventing food poisoning and botulism. Although the positive effect of nitrites on meat has been flagged, this curing agent involves the potential formation of nitrosamines through the reaction with secondary amines, which are compounds with teratogenic, mutagenic and carcinogenic effects (Cassens, 1997). Previously, Bogovski and Bogovski (1981) investigated the risk of cancer induced by the nitrouscompounds in animal species, concluding that these substances are potent carcinogens.

In the last few years, there have been proposals put forward to control and reduce the maximum authorized amount of nitrites permitted in meat products. In the EU, potassium and sodium nitrite and nitrate are authorized for use in different meat products (Commission Regulation (EC) No 1129/2011). Maximum added or residual amounts are established depending on the meat product (Directive 2006/52/CE). When the maximum amount of added nitrite is regulated it should not exceed 150 mg/kg, however, in some products nitrite is added by rubbing on the surface manually or in a tumbler (e.g. dry-cured ham maximum residual 100 mg/kg or dry-cured bacon 175 mg/kg) or brine-cured (Wiltshire bacon and toucinho maximum residual 175 mg/kg). Thus, it means that nitrite is at very high concentrations on the surface until equalization.

Since it is difficult to control the level of endogenous factors, such as amino acids and amines, it would be necessary to evaluate the effect of the reduction in the nitrite added to products and to gain greater knowledge of the reaction and process conditions while preserving the product safety. For this reason, it is essential to control the curing process, i.e. the amount of nitrites, the curing time and the main factors governing nitrite penetration into meat. The transfer mechanism of both nitrite ion and sodium through the meat structure is an interesting aspect in meat processing technology. The transport phenomenon in the meat brining operation, defined by the transfer of salts and water, is complicated and depends on aspects such as salt concentration, temperature, pH and meat fibre direction (Barat et al., 2011; Boudhrioua et al., 2009; Gravier et al., 2006, 2009).

One of the best ways to learn about the factors governing this process is by using mathematical models, which may represent the process, explain the observed data and predict the behaviour under different conditions (Mulet, 1994). Diffusion models are usually applied to describe mass transfer in food. Diffusion is the most

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Nomenclature

C	concentration of nitrite or water (kg/m^3)	D_{N0}	pre-exponential factor in equation 11 (m^2/s)
C_e	equilibrium concentration of nitrite or water (kg/m^3)	D_{w0}	pre-exponential factor in equation 12 (m^2/s)
$\overline{C}_s$	average nitrite concentration (kg/m^3)	D_{we}	effective diffusivity of water (m^2/s)
C_0	initial concentration of nitrite or water (kg/m^3)	E_{Na}	activation energy for nitrite (kJ/mol)
C_{se}	average equilibrium nitrite concentration (kg/m^3)	E_{wa}	activation energy for water (kJ/mol)
C_{s0}	average initial nitrite concentration (kg/m^3)	L	length of the cylinder (m)
$\overline{C}_w$	average moisture content (kg water/kg dry matter)	R	ideal gas constant (8.31 J/mol K)
C_{we}	average equilibrium moisture content (kg water/kg dry matter)	R^2	explained variance
C_{w0}	average initial moisture content (kg water/kg dry matter)	T	temperature (K)
D_e	effective diffusivity of nitrite or water (m^2/s)	t	time (s)
D_{Ne}	effective diffusivity of nitrite (m^2/s)	x	cartesian coordinate (m)

important mass transfer mechanism during salting (Barat et al., 2003; Wang et al., 2000). Effective diffusivity, which includes the effect of known hypotheses and unknown phenomena which are not included in the model, can be calculated by means of diffusion models. When modelling, this parameter can be considered constant (e.g. Gou et al., 2003; Gravier et al., 2006) or dependent on some process or product conditions. For example, Gravier et al. (2009) in a study on pork meat salting with a mixture of $NaNO_2$, KNO_3, and NaCl considered that the effective diffusion coefficient depended on NaCl concentration.

The diffusivity is a parameter to consider in the curing process since it affects the water content and, in turn, the salt penetration into the meat. It is significantly affected by operating temperatures. An increase in temperature raises the thermal energy of molecules, resulting in an increase in the diffusion rate of the molecules (Gou et al., 2003; Pinotti et al., 2002). Thus, the dependence of diffusivity on temperature is generally described by the Arrhenius equation.

The diffusion of sodium chloride (NaCl) and the influence of its concentration on the diffusivity of a mixture of salts (NaCl, $NaNO_2$ and KNO_3) in pork, beef and fish has been studied by different researchers (Graiver et al., 2006; Sabadini et al., 1998; Siro et al., 2009; Wang et al., 2000). Likewise, studies have been performed on the kinetics of the diffusion of sodium chloride during chicken meat curing (Volpato et al., 2007). Other studies show the influence of curing salts on the macro and microstructure of the treated product: for example pork meat immersed in NaCl brines of different concentrations (Graiver et al., 2005, 2009) or pork meat salted by immersion in brines of different compositions ($NaNO_2$, KNO_3 and NaCl) (Pinotti et al., 2000). Nevertheless, neither has the diffusive behaviour of sodium nitrite inside the meat been published, nor the effect of the curing temperature on the diffusion of this salt. On the other hand, due to the increase of the interest about reducing NaCl in meat products (Stollewerk et al., 2012), it is important to know the behaviour of isolated salts in the curing process, for better understanding the diffusion process of a mixture of salts. Therefore, for the purposes of contributing to an improvement in ham processing, the objective of this research was to study the effect of temperature on the diffusion kinetics of sodium nitrite and water in the *Semimembranosus* muscle of pork leg.

2. Materials and methods

2.1. Raw material

Six pork legs, with an average weight of 9.6 ± 1.2 kg and a $pH_{45} > 6.0$ and pH_{24} of 5.9 ± 0.1, were selected from a local slaughterhouse. All the pork legs came from different animals obtained at a commercial slaughterhouse the day before the curing process began. The legs were packed in plastic film and stored at 2 ± 1 °C for between 13 and 14 h before separating the *Semimembranosus* muscle (SM). The SM muscle was separated from each leg and fourteen cylinders, 8.4 cm in height and 2.4 cm in diameter were obtained from each muscle, keeping the orientation of the meat fibres parallel to the cylinder axis (Fig. 1). Thirteen of the fourteen cylinders obtained from each muscle were used for curing with sodium nitrite ($NaNO_2$) and the remaining cylinder was used to characterize the initial conditions of the meat.

2.2. Experimental conditions

The cylinders were weighed and their side faces were subsequently covered with a PVC film to prevent moisture loss. Each cylinder was hung from one of its bases and the other one was in contact with a brine saturated with sodium nitrite ($NaNO_2$). The brine was prepared with an excess of $NaNO_2$ in order to compensate the amount absorbed by the meat. The saturated brine and the cylinders were placed randomly into curing chambers at 2, 7 and 12 °C (thirteen cylinders per chamber) with 95 ± 1.5 % relative humidity.

In order to control the temperature, the curing chambers were placed inside a chamber with controlled temperature and relative humidity. Inside the curing chambers, the relative humidity was maintained at around 95% by means of a saturated brine of KNO_3. The measurement of temperature and relative humidity

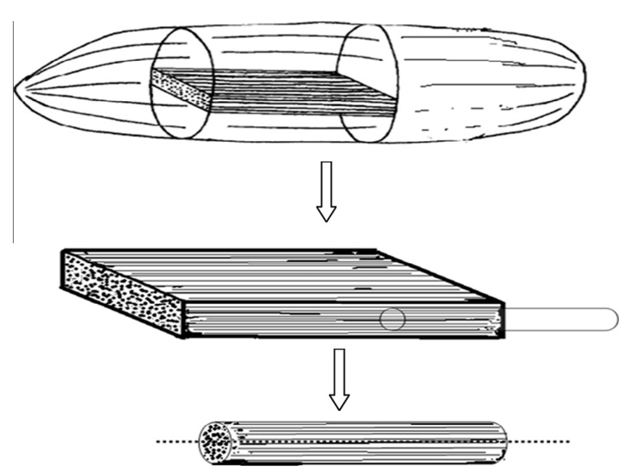

Fig. 1. Meat fibre orientation in the samples from the *Semimembranosus* muscle.