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Thermodynamic approach of meat freezing process

M. Castro-Giráldez, N. Balaguer, E. Hinarejos, P.J. Fito *

Instituto Universitario de Ingeniería de Alimentos para el Desarrollo, Universidad Politécnica de Valencia, Camino de Vera s/n, 46022 Valencia, Spain

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A B S T R A C T

Frozen storage is a method widely implemented in meat industry in order to maintain the nutritional value and sensorial characteristics of meat products. The aim of this research was to implement and validate the use of the infrared technique as a non-destructive control tool to monitor the physicochemical phenomena that occurred during the freezing stage. This enables to evaluate the final impact of this operation in a complex system such as meat. To do this, the evolution of the freezing process in pork loin (*Longissimus dorsi*) was followed by a thermographic camera Optris PI® 160 thermal imager (Optris GmbH, Berlin, Germany), whose spectral infrared range of wavelength is comprised between 7.5 and 13 μm. The results obtained have demonstrated the existence of a chemical potential gradient which caused an internal flux of water. In turn, as a result of nucleation phenomena and the influence of the surface tension existent, a new water chemical potential gradient appeared, leading to the displacement of water molecules towards the ice agglomerates. This provoked the progressive dehydration of the tissue areas immediately close to the ice crystals. Micrographs obtained in different positions of the meat tissue confirm this theory.

Industrial relevance: Currently, there is a significant gap in the knowledge of the complex phenomena that occurred during food freezing. This research develops a thermodynamic model which provides an accurate explanation and a new insight of the main mechanisms involved in the meat freezing process. Moreover, this model enables to leave a proof of the real structural impact that occurred in the muscular tissues, as a consequence of the generation of ice crystals and agglomerates. In order to carry out this research, the thermal imaging (TI) technique has been used. This is an innovative and emergent technology whose popularity and use at the food industry has experienced a significant growth in recent years. The results obtained represent a starting point for the future development of on-line cold chain monitoring systems in the food industry. The aim is no other than to provide the necessary basis to meet current demands for food quality and safety.

1. Introduction

Freezing is an important preservation method used for extending the shelf life of meat and meat products since compared with other methods; it leads to a minimal loss of quality during long-term storage at low temperatures (Soyer, Özalp, Dalmis, & Bilgin, 2010). From an engineering point of view, the freezing process is an unsteady-state heat transfer phenomenon in which the food loses heat by convection through its surface and by conduction at its interior (Rahman, Machado-Velasco, Sosa-Morales, & Velez-Ruiz, 2008). The most important factor affecting the freezing process is food composition, where the water content, the characteristic of other food components, soluble and insoluble solids; and other factors such as specific heat, enthalpy and coupled transport phenomena of mass and energy are important (Jie, Lite, & Yang, 2003). Additional influencing aspects are food microstructure, particle size, porosity and certain biological aspects like species, age and maturity (Devine, Bell, Lovatt, Chrystall, & Jeremiah, 1996; Hamdami, Monteau, & Le Bail, 2004).

More specifically, the freezing process consist of freezing, frozen storage and thawing. Freezing involves lowering the product temperature generally to −18 °C or below (Fennema, Powrie, & Marth, 1973, chap. 1). The temperature reduction process can be divided into three distinct phases: a pre-cooling or chilling phase in which the material is cooled from its initial temperature to the freezing point temperature (T_f), a phase change period which represents the crystallization of most of the water; and a tempering phase in which the product reaches the final established temperature (eg: −18 °C). It is noteworthy that typical cooling curves show at the beginning of process an abrupt rise in temperature due to liberation of heat of fusion after an initial supercooling. This stage represents the onset of ice crystallization. Once the crystal embryos exceed the critical radius for nucleation, the system nucleates and releases its latent heat faster than the heat removed from the system. The temperature then increases instantly to the initial freezing temperature (T_f) (Rahman, 1999; Rahman & Driscoll, 1994; Rahman et al., 2008) in order to start the period in which most of the ice formation occurs.

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* Corresponding author.
E-mail address: pedfisu@tal.upv.es (P.J. Fito).

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Nomenclature

E_j	flux energy emitted by a body surface ($kg\ s^{-3}$)
F	geometric factor (−)
a_j	activity of the chemical specie j (−)
R	ideal gases universal constant ($J\ mol^{-1}\ K^{-1}$)
T	temperature (K)
s	molar partial entropy ($m^2\ kg\ s^{-2}\ K^{-1}\ mol^{-1}$)
P	absolute pressure (Pa)
r	radio (m)
q	heat ($m^2\ kg\ s^{-2}\ mol^{-1}$)
Cp	specific heat ($m^2\ s^{-2}\ K^{-1}$)
V	variation of volume (l)
L	length (m)
n	number of moles (mol)
M	mass (kg)
A	surface (m^2)

Greek alphabet

ε_j	emissivity of a body (−)
σ	Stephan–Boltzmann constant ($W\ m^{-2}\ K^{-4}$) or surface tension of ice ($kg\ s^{-2}$)
Δ	variation of a variable
μ_j	chemical potential of the specie j ($J\ mol^{-1}$)
ν_j	molar partial volume of the specie j ($L\ mol^{-1}$)
ρ	density (kg/m^3)

Subscripts and superscripts

T	total
obj	object
sur	surroundings
air	air
s	sample
ref	reference
w	water
UFW	unfreezable water
f	freezing
i	ice
m	meat

The main advantage of modelling the freezing process is to contribute to understand the complex changes motivated by the variations of temperature and the changes in the quantity and availability of water in a food system. It also assists in identifying food's stability during storage, as well as in selecting a suitable condition for processing (Rahman, 2006).

Food engineers are interested in predicting cooling and freezing times in order to estimate the refrigeration requirements for freezing systems and to design the necessary equipment for effective and rational processing (Delgado & Sun, 2001). Minimization of the energy requirement, reliability safety and quality of the product must also be considered. Models available to describe the freezing process can be divided into two main groups: heat transfer models and coupled heat and mass transfer models. A good number of studies of coupled heat and mass transfer have included experiments for either establishing the control of physical properties for analysis or to validate multi-convective diffusion models (Goldstein et al., 2010). Nonetheless, despite the progress made in the modelling of freezing, there is still a large gap in the field of modern thermodynamics. Indeed today there are no conclusive studies to control simultaneously both, the transport phenomena and the phase and structural changes produced as consequence of the application of a heat treatment.

Being able to develop a thermodynamic model in the meat industry, in order to describe the physicochemical phenomena during freezing, is intrinsically related to the implementation of on-line control methods that ensure an adequate shelf life of the product. In this sense, nowadays in the meat industry the use of a cutting-edge technology for the processing control is promoted: the thermal imaging (TI).

TI is an excellent method for studying the heat transfer in multicomponent systems such as the meat muscle. It is a technique that converts the radiation emitted by a body surface into temperature data without establishing contact with the object (Vadivambal & Jayas, 2011). The infrared radiation emitted by a body surface contains characteristic information of the material composition and its properties (Giorleo & Meola, 2002). The use of this information through an appropriate system of data acquisition and treatment allows us to determine and control certain properties which are difficult to measure otherwise. In fact, due to the enormous potential of the infrared thermography as a tool of control and design (Gowen, Tiwari, Cullen, McDonnell, & O'Donnell, 2010), the food industry is investing effort and money to adapt it to different processing lines, especially in the agriculture sector (Alchanatis et al., 2006; Chaerle & Van der Straeten, 2000; Fito, Ortolá, De los Reyes, Fito, & De los Reyes, 2004; Lamprecht, Schmolz, Blanco, & Romero, 2002; Oerke, Steiner, Dehne, & Lindenthal, 2006; Stajnko, Lakota, & Hocevar, 2004; Sugiura, Noguchi, & Ishii, 2007).

Regarding the applicability of this technique in meat industry, several studies have shown that it is feasible to use the TI for the assessment of pork and raw ham quality (Costa et al., 2007), as well as for determining and controlling the evolution of the internal temperature of cooked chicken meat (Ibarra, Tao, Cardarelli, & Shultz, 2000; Ibarra, Tao, Walker, & Griffis, 1999; Ibarra, Tao, & Xin, 2000). The aim of this work is to determine the effect of internal water flux in meat freezing process and evaluate the use of the infrared technique to control the meat freezing process.

2. Materials and methods

2.1. Experimental procedure

Experiments were carried out using ten loins (*Longissimus dorsi*) collected at 6 h post-mortem from the slaughterhouse “La cope” placed in Torrente, Valencia. Prior to freezing, several samples were extracted from each loin in order to undertake a preliminary analysis based on the raw meat quality characterization (pH_{24h}, L^*_{24h} value and drip loss), moisture and water activity measurements. Concurrently, a DSC study was made in order to calculate the specific heat of meat during the freezing process. Finally, a microstructural study was performed by low-temperature scanning electron microscopy (Cryo-SEM) either in fresh and frozen samples. Once the sampling was done, every sample was properly labelled, sealed with parafilm and kept at 4 °C in an incubator Hotcold-M (JP Selecta®) until the corresponding analysis were made.

Pork loins, were classified based on pH_{24h}, $L_{24h}{}^*$ value and drip loss, according to the classification proposed by Toldrá and Flores (2000). The pH of samples was measured with a punch pH-metre S-20 SevenEasy^{TM} (METTLER TOLEDO, Spain) at 24 h after slaughtering. Drip loss determination was undertaken following the method proposed by Honikel (1998). The colour of samples was measured by the surface reflectance spectra in a spectrocolorimeter Minolta CM-3600D (Minolta Co. Ltd., Japan) at 24 h post-mortem. The colour coordinates CIE L*a*b* (CIE, 1978) were instrumentally calculated based on D65 illuminant and 10° observer. Water content was determined by drying at 110 °C at atmospheric pressure, following the ISO 1442 (1997), for meat products. Finally, the surface water activity (a_w) was determined by a dew point hygrometer Decagon (Aqualab®, series 3 TE), with precision ±0,003. Measurements were made in structured samples (not minced), thus a_w obtained is considered to be surface a_w. All the measurements were made in triplicate.