



# Migration of smoke components into pork loin ham during processing and storage



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## ABSTRACT

The migration of smoke components into pork ham during smoke processing was measured and estimated by using the hypothetical equilibrium absorption at the surface of the casing ( $C_{max}$ ) via Fick's equation. The temperatures of the heating medium, surface, and core of the product were monitored. 2,6-Dimethoxyphenol was used as an index for smoke components and was evaluated by HPLC. Empirical equations used to predict the concentration of smoke components ( $C_{We}$ ) generated inside the smokehouse based on the weight of burned wood were obtained.  $C_{We}$  values were used to estimate the migration of smoke components into ham at several internal positions and agreed well with the measured values, regardless of the initial weight of wood. Smoke components adhered to the surface of the ham casing and then migrated to the interior of the ham, but did not reach the core even after 7 days of storage.

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## 1. Introduction

Smoke processing has been used as a preservation technique since antiquity, owing to the antimicrobial and antioxidant properties of wood smoke. Coupled with salting and drying, smoke processing decreases the activity of microorganisms. Simultaneously, wood smoke imparts desirable organoleptic characteristics such as a smoky flavor. In ham production, smoke was reported to impart some volatile components to the product that inhibited bacterial growth (Poligne et al., 2001) and added a smoky flavor (Arboix, 2004).

A smoky flavor and color result from the direct deposition of the smoke particles onto the surface of food. In addition, the flavor and color penetrate the skin or product surface, since smoke can penetrate organic surfaces (Herring and Smith, 2012). Maga (1988) reported that upon heating, a chemical reaction occurs between carbonyls within smoke vapor and individual amino acids that make up meat proteins. Such chemical reactions cause non-enzymatic browning that is similar to the Maillard browning reaction. While the browning reaction may take place at lower temperatures, it occurs more rapidly at increased temperatures; thus, darker colors or more intense flavors will be obtained at higher temperatures. Smoked meat is widely accepted to have an

enhanced taste, texture, and flavor, but the intensity may change depending on the kind of meat and other factors. Smoke is imparted in meats at different rates depending on the air flow into the smokehouse, surface moisture of the meat, temperature, and humidity of the smokehouse (Herring and Smith, 2012). The exact composition or ratio of gases and solids within the smoke stream depends on the type and moisture content of wood, rate and temperature of heating/burning, and other factors such as air flow.

Herring and Smith (2012) reported that humidity in the smokehouse, resulting from moisture in the wood or product, environmental conditions, and the relationship between the wet and dry bulb settings of the oven, should be monitored and reduced because condensates prevent smoke from adhering to the product's surface and the water-soluble components of smoke will mix with the condensate of the meat and drip off the meat. Thus, if the humidity is too high, the color of the product will be dark and muddy as opposed to mahogany or red. However, if the humidity is too low, the product casing will harden. During case hardening, the product will form a thick, dry exterior layer, since the proteins are denatured and cannot bind as much water. If the surface is too dry, smoke will not adhere well and will not penetrate the product, which will prevent a uniform smoke flavor.

Additionally, meat products should be heated to remove surface moisture as it causes protein coagulation and the development of a tacky surface, which increases smoke deposition and adherence. However, meat should not be heated too rapidly as this will cause

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### Nomenclature

|                  |                                                                                                                       |         |                                                                                            |
|------------------|-----------------------------------------------------------------------------------------------------------------------|---------|--------------------------------------------------------------------------------------------|
| $A$              | smoke component absorbance dissolved in water (-)                                                                     | $L$     | thickness of the casing (m)                                                                |
| $C$              | smoke component concentration in the ham ( $\mu\text{g g}^{-1}$ )                                                     | $r$     | radial position in the cylindrical shape (m)                                               |
| $C_c$            | smoke component concentration attached at the casing ( $\mu\text{g g}^{-1}$ )                                         | $R$     | radio of the ham (m)                                                                       |
| $C_{\text{max}}$ | amount of the hypothetical concentration equilibrium absorption at the surface of the casing ( $\mu\text{g g}^{-1}$ ) | $T_a$   | ambient temperature ( $^{\circ}\text{C}$ )                                                 |
| $C_w$            | smoke component concentration in the smokehouse dissolved in water ( $\mu\text{g g}^{-1}$ )                           | $U$     | overall mass transfer coefficient ( $\text{m s}^{-1}$ )                                    |
| $C_o$            | initial smoke concentration ( $\mu\text{g g}^{-1}$ )                                                                  | $x$     | position in the flat plate shape (m)                                                       |
| $D$              | diffusion coefficient in the ham ( $\text{m}^2 \text{s}^{-1}$ )                                                       | $z$     | axial position in the cylindrical shape (m)                                                |
| $D_c$            | diffusion coefficient in the casing ( $\text{m}^2 \text{s}^{-1}$ )                                                    | $\beta$ | mass transfer coefficient for the surface of the ham from the casing ( $\text{m s}^{-1}$ ) |
| $h_m$            | mass transfer coefficient ( $\text{m s}^{-1}$ )                                                                       |         |                                                                                            |

case hardening and fat will migrate outside (Herring and Smith, 2012).

Smoke generation is a result of pyrolytic changes in wood. Pyrolysis is a type of incineration that breaks down organic matter via chemical reactions in anaerobic environments. Smoke contains many different components such as aldehydes, ketones, alcohols, acids, hydrocarbons, esters, phenols, and ethers, which are deposited on the surface and later penetrate meat (Gomez-Estaca et al., 2011). Analysis of smoke components (Maga, 1995) revealed that smoke contains around 400 components. However, understanding the behavior of all components is difficult, because the absorption of the main components is commonly utilized as an index for practical uses. Oota et al. (1997) reported the use of formaldehyde as well as carbonyls, acids, and phenols, as indices for smoke components. Several volatile components have been isolated from smoke vapor and smoked meats. For example, Zhu et al. (1993) isolated 2,6-dimethoxyphenol, also known as syringol, which has been recognized to impart a smoky odor and woody/herby flavor.

A few theoretical and experimental studies have been carried out to understand the transfer of solutes through meat and meat product matrices, as in ham, in which water and salt diffusion takes place in addition to the migration of smoke components (Costa-Corredor et al., 2010; Sebastian et al., 2005). However, little is known regarding the migration of smoke components during smoke processing. Chan et al. (1975) determined that the kinetics of smoke deposition is affected by the smokehouse temperature, humidity, and air flow. They evaluated the effects of these conditions on temperatures within the product. Sanches-Silva et al. (2007) studied the migration of a model migrant (diphenylbutadiene) from packaging film into the interior of meat products, and concluded that migration increased with increasing fat content and storage temperatures. However, the effect of the concentration of smoke components inside the smokehouse on the migration of smoke components remains to be elucidated. In this study, the migration of smoke components into ham was experimentally analyzed via HPLC experiments using a smoke component index. The concentrations of smoke components inside the smokehouse were calculated using empirical equations based on the amount of burned smoke wood to mathematically estimate the migration using the hypothetical equilibrium absorption at the surface of the casing ( $C_{\text{max}}$ ). Finally, the migration behavior during storage was experimentally evaluated.

## 2. Materials and methods

### 2.1. Raw material

Pork sirloin was used as the sample. Meat was purchased on the day of sample preparation, in the rigor mortis state, and was stored

at 4 °C. The fat was removed carefully from the initial block of 1000 g ( $\approx 150 \times 130 \times 60 \text{ mm}^3$ ) to obtain premium standards (MHLW, 2008). Thus, the final weight of the refined block was approximately 700 g. The refined samples had moisture and crude fat contents of  $54.9 \pm 0.2\%$  and  $6.2 \pm 0.1\%$  (wb), respectively, which were measured according to AOAC (1995).

### 2.2. Manufacturing process of pork ham

A  $750 \times 650 \times 700 \text{ mm}$  smokehouse (laboratory level, Hanaki Industry Co., Ltd., Japan) was used. The air flow inside the smokehouse is shown in Fig. 1. The steam used during wet smoking and steam heating steps was generated by a boiler (SAMSON Steam Boiler FBC-60S, Sindi60, Japan) at an evaporation rate of  $60 \text{ kg h}^{-1}$ . The thermal schedule used in the manufacturing process of pork ham was recommended by a Japanese manufacturer (Hanaki Engineering Corporation).

#### 2.2.1. Curing

The refined pork block was cured in 1000 mL of curing solution prepared with 10.8% w/w of curing mix (ham salt agent for meat products MIX # 10, Daiichikasei, Daiichi Co., Japan). The ingredients of the curing mix are shown in Table 1. Soaking was performed at 3–4 °C for 1 week. In addition, for faster penetration,

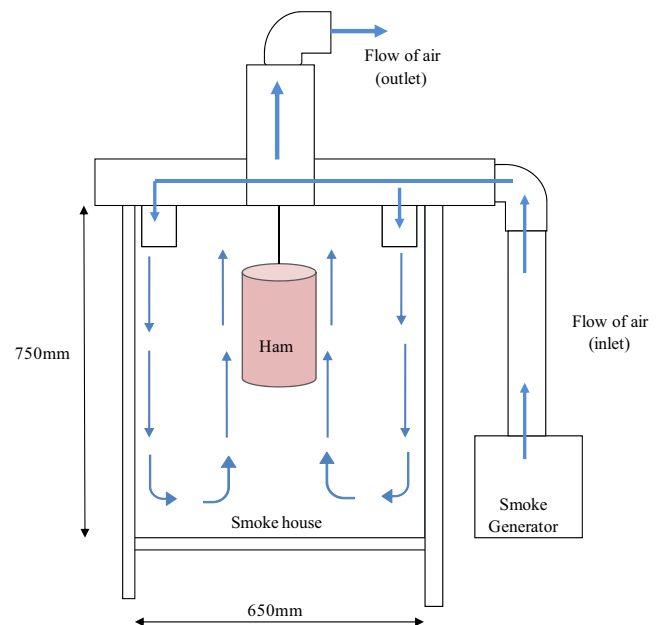


Fig. 1. Schematic diagram of the smokehouse and air flow.

**Table 1**  
Ingredients of the curing solution used to cure the loin ham.

|                                   |        |                              |       |
|-----------------------------------|--------|------------------------------|-------|
| Sodium polyphosphate              | 5.00%  | L-monosodium glutamate       | 2.80% |
| L-ascorbic acid                   | 2.80%  | Tetrasodium pyrophosphate    | 1.70% |
| Pyrophoric acid 2 hydrogen sodium | 1.70%  | Sodium nitrite               | 0.55% |
| Cyclodextrin                      | 0.55%  | Spices extract               | 0.01% |
| Arabic gum                        | <0.01% | Food material <sup>a,b</sup> | 84.8% |

<sup>a</sup> Food material contents: salt, grape sugar, plain sugar, and starch syrup.

<sup>b</sup> The total content of salt in the food material is 56% approximately.

the same curing solution was also directly injected (in eight different positions) into the meat using a needle and a 50 mL syringe, which was filled with a certain amount of curing solution in the proportion of 0.15:1 with respect of the weight of the meat sample, prior to immersion in the curing solution, as recommended by Carlier et al. (1996). The pH and Na concentration of the curing solution were 7.13, and 6.18% w/w, respectively.

### 2.2.2. Desalting and packing

After curing, the meat was immersed into soaking water without salt to remove excess salt from the surface layer. The soaking process (MAG-MIXER stirrer chip, Yamato Mfg. Ltd., Japan) was conducted twice under forced convection using 5 L of distilled water for 30 min at 4 °C. The process was carried out inside a low-temperature incubator (IN600 Ltd. Yamato Scientific Ltd., Japan); the temperature of the air was 4 °C. Then, the meat was stuffed in a fibrous casing with a smoke permeable film (Meatlonn, Futamura Chemical Co., Ltd., Japan) and packed using a filling machine (Jet Horn, Jet Net Corp., USA) to ensure that there was no gap between the casing and meat. Finally, the ends of the sample were clipped using a tipper tie machine (SPR465L, Dover Company, USA).

### 2.2.3. Dry processing

The stuffed meat was hung using a kite string in the center of the smokehouse. Dry processing, with a velocity of the air of  $1.8 \text{ m s}^{-1}$ , was conducted in two steps: a first drying under a dry-bulb temperature of 60 °C for 30 min (38% of relative humidity-RH), and a second drying under a dry-bulb temperature of 70 °C for 90 min (22% of RH).

### 2.2.4. Smoke processing (smoking step)

The smoking step included two basic steps: a dry-smoking step, which was conducted under a dry-bulb temperature of 70 °C for 10 min, and a wet-smoking step conducted after reducing the temperature of the smokehouse by setting a 56% of RH for 10 min (temperature of the wet-bulb: 58 °C). The air flowed at an average speed of  $1.8 \text{ m s}^{-1}$ . Cherry wood sticks (Shinsei Sangyo Co. Ltd., Japan) were used as the smoking material, which are commercial compacted products of cherry wood sawdust in stick shape. The generator of the smokehouse was programmed to reach 350 °C. The steam pressure was adjusted to 0.1 MPa for the wet smoking step.

Herring and Smith (2012) detailed the reasons to choose a lower temperature in the smoke generator for the combustion of the smoke wood. Hardwoods, as the case of cherry wood, typically consist of 40–60% cellulose and 20–30% of both hemicellulose and lignin. This composition is important since pyrolysis of these components occurs at different temperatures. Hemicellulose pyrolysis occurs from 200 °C to 250 °C, cellulose pyrolysis occurs from 280 °C to 320 °C, and lignin pyrolysis occurs at 400 °C. However, volatile compound generation is dependent upon temperature. Carbonyls and phenols are generated from 200 °C to 600 °C with phenol production decreasing as the temperature exceeds 500 °C. Acid production is highest at 300 °C, but decreases as the temperature increases over 300 °C. Moreover, is necessary to avoid the

risk of polycyclic aromatic hydrocarbons (PAHs) production, which are produced during lignin pyrolysis and generated over a wide temperature range (400–1000 °C).

### 2.2.5. Steam heating

After the smoke processing, the meat was heated for 40 min at a RH of ~100% (temperature of the wet-bulb: 78 °C). Accordingly, the central temperature of the product increased to 70 °C. This steam heating schedule was selected to meet the regulations of the Japanese Food Sanitation Law as was recommended by MHLW (2008). For meat products, such as sirloin ham, the core temperature of the product should be at least 63 °C for more than 30 min or its equivalent.

## 2.3. Temperature measurements

In this study, four measurement points were considered including the surface of the samples captured using a T-type thermocouple (sheet type,  $70 \times 7 \text{ mm}$ ), the core of the loin ham captured using a T-type thermocouple ( $\phi = 3.2 \text{ mm}$ ), and the center of the smokehouse, as well as the center of the smoke generator using two K-type thermocouples ( $\phi = 1.2 \text{ mm}$ ). A personal computer, datalogger (Thermodac 5030A, Eto Denki Co., Japan), and software (Thermodac-E/Ef 2.6, Eto Denki Co.) were used to collect the temperature data.

### 2.4. Determination of the amount of smoke wood burned during smoke processing

The amount of smoke wood burned in 20 min was measured using the same thermal schedule as described above in Section 2.2.4. Three initial amounts of smoke wood (20, 40, and 80 g) were used. Before the combustion process, the smoke wood was kept overnight in a glass desiccator. The initial weight of the smoke wood (27% of moisture content, wb) was determined and then it was placed inside the generator. The desired moisture content of the smoke wood is in accordance to the recommendation of Guillén and Ibargoitia (1996), who claimed that moisture content in the range of 20–30% causes reduced PAHs production, slow wood combustion, and increased adherence of smoke to the product surface. With the exception of during the 10 min of pre-heating step, the amount of smoke wood burned was measured every 5 min for 20 min. Afterwards, the smoke wood was immediately removed from the generator and was cooled in water of a known volume. Thus, the final weight of burned smoke wood was controlled. The difference in weight between the smoke wood before and after burning was defined as the amount of the smoke wood burned during smoke processing ( $n = 5$ , for each initial smoke wood weight).

## 2.5. Determination of the concentration (C) of smoke components in ham

### 2.5.1. Preparation of the extract component

The position of the smoke components inside the ham was examined via a radial distribution. The cylinder shape of the ham

(70 × 120 mm) was divided into three parts in the direction of height, and only the middle portion (70 × 30 mm) was used for the determination. The radial direction was divided into concentric circles and the center positions of the obtained regions (0–10, 10–20, 20–30, 30–32.5, and 32.5–35 mm from the ham core) were used for the sample extraction (5, 15, 25, 31.3, and 33.8 mm from the ham core). The procedure used for the smoke component extraction was carried out according to the method suggested by Suzuki and Motosugi (1990). From the selected positions, 2 g of sample was collected and homogenized with the extraction solution prepared with ethanol (60% v/v), and was stirred for 15 min at 25 °C. After the extraction of the homogenate, 50 mL of the extraction solution was added against. After a constant volume was obtained, the sample was filtered using a 0.45 µL filter syringe. Then, the sample was submitted to HPLC analysis. Evaluations were conducted over 7 days. In order to prevent the drying of the surface and the outflow of smoke components, samples were subjected to vacuum packaging with a laminated retort pouch (PET12/AL9/NY15/CP60; HR-Type, Meiwa Sanshou Co. Ltd., Japan) after preparation and were stored at 4 °C.

### 2.5.2. Analysis of smoke components by HPLC

High performance liquid chromatography (HPLC; L-4200 UV-VIS Detector, Hitachi, Ltd., Japan) was used. The column (CAPCELL PAK C18 4.6 φ × 150 mm, Shiseido, Japan) was set at 55 °C. A 20 µL aliquot of the test solution was prepared with methanol:distilled water (50:50 v/v) and the pH was adjusted to 1.48 with phosphoric acid; then it was injected into the column via a pump (L-600, Hitachi, Ltd., Japan). The injection was conducted at a flow rate of 0.5 mL min<sup>-1</sup>. The wavelength measurements were conducted at 268 nm. To evaluate the migration of the smoke components, 2,6-dimethoxyphenol was used as an index. The same index was used by Suzuki and Motosugi (1990). A calibration curve was generated.

### 2.6. Determination of $A$ and $C_w$

First, a beaker containing 50 g of distilled water was placed in the center of the smokehouse, in the same position where ham is usually placed. After the completion of the smoking step following the parameters shown in Table 2, the beaker was removed and the maximum absorption wavelength ( $A$ ) at 275 nm was measured using a spectrophotometer (UV-1800, Shimadzu Corporation, Japan). Several initial amounts of smoke wood were used during the 20 min smoking step. To measure the concentration of smoke components dissolved in water ( $C_{wm}$ ), HPLC was used in the same way as described for  $C$  (smoke component concentration in the ham (µg g<sup>-1</sup>)) in Section 2.5.2. An estimated value,  $C_{we}$ , was derived from the relationship with burned smoke wood, as explained in the results section.

**Table 2**  
Parameters used during smoking step for the determination of the amount of the smoke absorbance ( $A$ ).

| Initial weight of the smoke wood (g) | Smoking time (min) | Temperature (°C) |          |
|--------------------------------------|--------------------|------------------|----------|
|                                      |                    | Dry-bulb         | Wet-bulb |
| 40                                   | 10                 |                  |          |
| 20                                   | 20                 |                  |          |
| 40                                   | 20                 | 70               | 58       |
| 80                                   | 20                 |                  |          |
| 80 <sup>a</sup>                      | 40                 |                  |          |

<sup>a</sup> Smoke wood combination: 40 g + 40 g. The second 40 g of smoke wood was inserted after 20 min.

### 2.7. Analysis of smoke component migration

#### 2.7.1. Physical model

A mathematical estimation of the migration of smoke components in ham was conducted. The shape of the ham was assumed to be cylindrical. The cylindrical sample was considered to be 70 mm in diameter and 120 mm in length.

#### 2.7.2. Governing equations

Using the diffusion equation based on Fick's law (Eq. (1)), the diffusion of the smoke components during smoke processing was analyzed in 2D (two-dimensional coordinates). Assuming a uniform concentration of smoke around the ham, the smoke components were considered to flow over the entire surface of the ham.

$$\frac{\partial C}{\partial t} = \frac{1}{r} \left\{ \frac{\partial}{\partial r} \left( rD \frac{\partial C}{\partial r} \right) + \frac{\partial}{\partial z} \left( D \frac{\partial C}{\partial z} \right) \right\} \quad (1)$$

Initial conditions

$$t = 0, \quad C = C_0 = 0$$

As a boundary condition inside the ham

$$(1) \quad \frac{\partial C}{\partial r} = 0 \quad \text{at } r = 0 \quad (2)$$

$$\frac{\partial C}{\partial z} = 0 \quad \text{at } z = 0 \quad (3)$$

$$(2) \quad -D(\partial C/\partial r) = U(C_{\max} - C) \quad \text{at } r = R \quad (4)$$

$$(3) \quad -D(\partial C/\partial z) = U(C_{\max} - C) \quad \text{at } z = Z \quad (5)$$

where  $C$  (µg g<sup>-1</sup>) is the concentration of smoke components in the ham,  $D$  (m<sup>2</sup> s<sup>-1</sup>) is the diffusion coefficient of smoke components in the ham,  $r$  (m) is the radial position in the cylindrical shape,  $z$  (m) is the axial position in the cylindrical shape, and  $C_{\max}$  (µg g<sup>-1</sup>) is the hypothetical equilibrium absorption of smoke components when sufficient time has elapsed.

For the analysis of the diffusion of the smoke components, the diffusion through the casing must be considered. Thus, to obtain the overall mass transfer coefficient  $U$  (m s<sup>-1</sup>), Eq. (6) was used:

$$\frac{1}{U} = \frac{1}{h_m} + \frac{L}{D_c} + \frac{1}{\beta} \quad (6)$$

where  $L$  represents the 0.1 mm thickness of the casing,  $h_m$  (m s<sup>-1</sup>) is the mass transfer coefficient from the smokehouse into the casing,  $D_c$  (m<sup>2</sup> s<sup>-1</sup>) is the diffusion coefficient of the smoke index into the casing, and  $\beta$  (m s<sup>-1</sup>) is the mass transfer coefficient for the surface of the ham from the casing.

#### 2.7.3. Estimation of $D_c$ and $C_{\max}$

During the smoking step, after the migration of the smoke components into the casing, the smoke components continued to penetrate the interior of the ham by diffusion. Therefore, to appropriately calculate the migration of the smoke components, the boundary condition of the migration into the casing should be considered.

A wet smoking step inside smokehouse for the ham casing was conducted in the same way as explained above in Section 2.2.4, by placing a silicon board (150 × 150 mm) at the same position of the ham. Four sheet pieces of fibrous casing (120 × 120 mm) that had been previously soaked in hot water were pasted on this silicon board (Fig. 2). The same thermal schedule as that used during

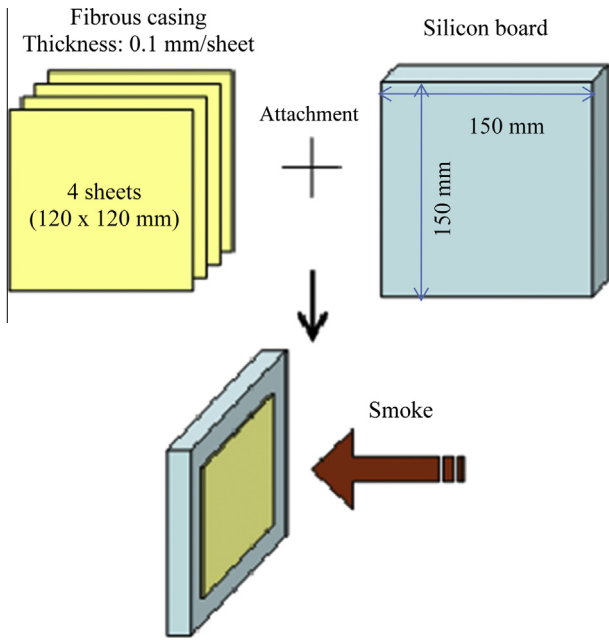


Fig. 2. Sample model for the determination of smoke component migration into casing.

the experiment that used 40 g of initial smoke wood was considered for the ham casing. The results after 5, 10, and 15 min of wet-smoking were evaluated. The migration of the smoke components into the casing was quantified using the smoke component index, by peeling off each casing sheet, one by one, from the inside of the silicon board. The  $D_c$  value was estimated accordingly.

For estimation purposes, theoretical values were approximated to fit the measured values. From Fig. 2, due to the silicon board, the migration of the smoke components was considered to occur in only one direction; for the simulations, the experimental system was assumed to follow the infinite flat plate model. Thus, Fick's diffusion equation in 1D (Eq. (7)) was used:

$$\frac{\partial C_c}{\partial t} = D_c \frac{\partial^2 C_c}{\partial x^2} \quad (7)$$

$t = 0, 0 \leq x \leq L, C_c = C_{ci}$  i: initial

$$(1) \quad \frac{\partial C_c}{\partial x} = 0 \quad \text{at } x = 0 \quad (8)$$

$$(2) \quad -D_c \left( \frac{\partial C_c}{\partial x} \right) = h_m (C_{\max} - C_c) \quad \text{at } x = L \quad (9)$$

A similar experiment as that described for the determination of  $D_c$  was conducted to determine the  $C_{\max}$  on the casing surface. The smoking step was 4 h, as no differences in the attachments of the smoke components were considered to occur after this time. An initial amount of 40 g of smoke wood was maintained by replacing the burned smoke wood every 10 min. The results are reported as the average of 3 determinations.

2.7.4. Solution procedure

The numerical analysis was performed using the finite element method under the aforementioned conditions. The developed model is based on the actual size of the ham. The Galerkin finite element method was used to solve the fundamental equations and to calculate the unsteady-state using a two-dimensional mass transfer profile. A Fortran program was used for this purpose.

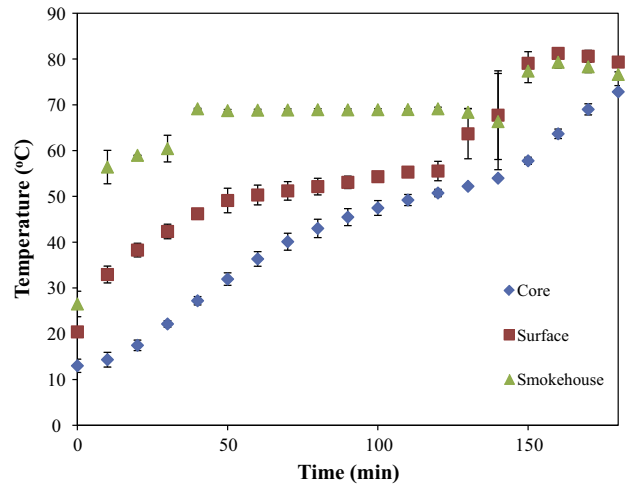


Fig. 3. Typical time-temperature profiles of pork loin ham and smokehouse during the entire smoking process. Bars indicate standard deviation from 5 determinations.

3. Results and discussion

3.1. Time-temperature profiles during smoke processing

The measured temperatures at the core and surface of the ham as well as the temperature of the smokehouse are presented in Fig. 3. The designed thermal schedule ensured that the temperature of the ham core remained below 60 °C until the steam heating step. This steam heating step started at the 140th min, thus might explain the large standard deviation at this time in Fig. 3. Yasui et al. (1981) recommended heating under low temperatures in order to prevent the denaturation of actin, and obtain a softer meat. Similar results were obtained in this study using the selected heating schedule, which facilitated a slow denaturation of the muscle proteins; thus, the texture of the muscle might be improved while maintaining the water-holding capacity (results not shown).

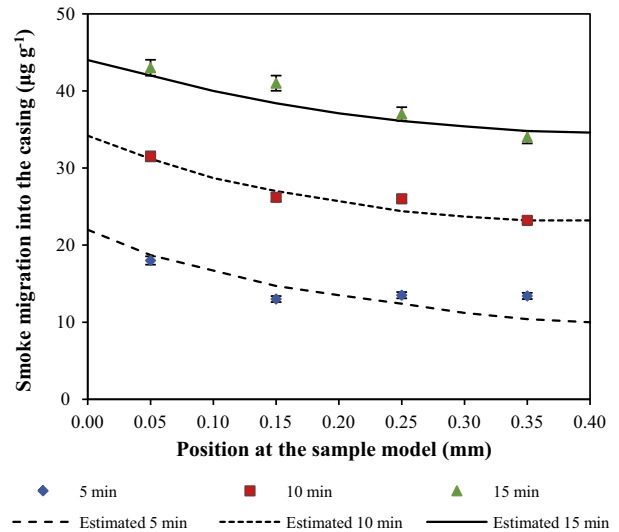


Fig. 4. Comparison of measured values of smoke component migration into casing (from sample model of Fig. 2) and estimated profiles using the calculated theoretical values (Eq. (7)) at different wet-smoking times. 40 g of smoke wood was used in all cases for the smoking step. Bars indicate standard deviation from 5 determinations.

3.2. Determination of the parameters for simulation of the smoke component migration into the casing

3.2.1. Estimation of  $C_{max}$ ,  $D_c$ , and  $h_m$

The smoke concentration inside the smokehouse is believed to significantly affect the migration of smoke components into the surface casing, taking in consideration that the air inlet was controlled and always was the same. Therefore,  $C_{max}$  was used to estimate the concentration of the smoke index in the casing of the ham. Using 40 g of smoke wood, a  $C_{max}$  value of  $153.5 \mu\text{g g}^{-1}$  was obtained. The migration of smoke components on the surface of the ham during the smoking step occurs because water is always impregnated at the superficial layer of the casing of the ham.

In Fig. 4, the smoke migration into the casing during the smoking step is presented; the position at 0 mm represents the surface exposed directly to smoke migration and the position at 0.4 mm represents the surface in contact with the silicon board (Fig. 2). The measured values, averaged at the center of each sheet, decreased from the surface to the interior of the ham. In other words, the smoke components attached to the surface and then migrated into the interior. Moreover, even though the thickness of the casing was very thin (0.1 mm), a reduced smoke migration into the internal sheets was observed.

The estimated profiles shown in Fig. 4 were generated by continuously changing the  $D_c$  and  $h_m$  values in Eq. (9), until the estimated profiles matched the measured profiles. As a result, the lowest absolute value of relative error (1.76%), obtained following a 10 min wet-smoking step, was obtained with a final  $D_c$  value of  $3.0 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$  and  $h_m$  value of  $1.29 \times 10^{-7} \text{ m s}^{-1}$ .

3.2.2. Estimation of  $D$ ,  $U$ , and  $\beta$

The diffusion coefficient,  $D$ , of 2,6-dimethoxyphenol in ham has not been published. Therefore, the modified diffusion coefficient of a similar substance was used. The diffusion coefficients obtained from five heating temperatures in the range of 40–70 °C for the migration of 1,4-diphenyl-1,3-butadiene (DPBD) into pork meat (Sanches-Silva et al., 2007 and Sanches-Silva et al., 2010) were used to estimate the diffusion coefficient at 65 °C using the Arrhenius equation:  $D = 1.47 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$ . This temperature

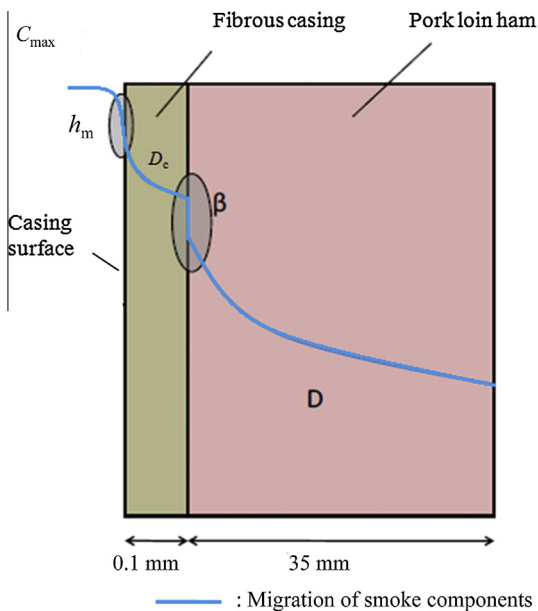


Fig. 5. Schematic diagram of the migration of smoke component into ham and the diffusion coefficients that were considered for the estimation of the overall mass transfer coefficient.

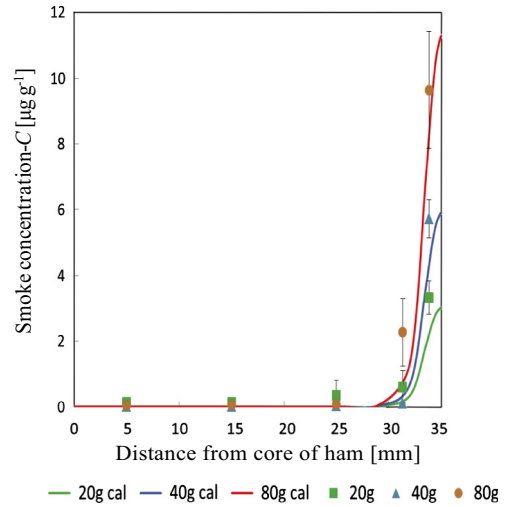


Fig. 6. Measured and estimated concentration of smoke components in pork loin ham according to initial weight of smoke wood used during 20 min smoking step. Bars indicate standard deviation from 5 determinations.

was considered as the average temperature reached during the steam heating step.

During the smoking step, for simulation effects, it was assumed that the smoke was absorbed on the casing fibers, and then diffused therein; thus, the smoke components proceeded into the ham surface from the casing. According to Eq. (6),  $U$  includes the  $h_m$ ,  $D_c$ , and  $\beta$  components, as shown in the schematic diagram in Fig. 5. To estimate  $U$ , the measured concentration of smoke components in the ham at different positions, using the results shown in Fig. 6 (for the case of 40 g), were compared to the estimated values by changing the  $U$  value in Eq. (5) until the estimated profiles matched the measured values. The lowest absolute value of relative error (1.46%) was obtained with a final  $U$  value of  $1.03 \times 10^{-9} \text{ m s}^{-1}$ .

Therefore, by using the previously estimated  $D_c$ ,  $h_m$ , and  $U$  values, the mass transfer coefficient for the surface of the ham from the casing,  $\beta$ , was calculated using Eq. (6) ( $\beta = 1.04 \times 10^{-9} \text{ m s}^{-1}$ ). Estimating the diffusion coefficients that contributed to the overall mass transfer coefficient to calculate the diffusion of the smoke components into ham revealed the significant contribution of the  $\beta$  value. Thus, even though a smoke-permeable casing was used,

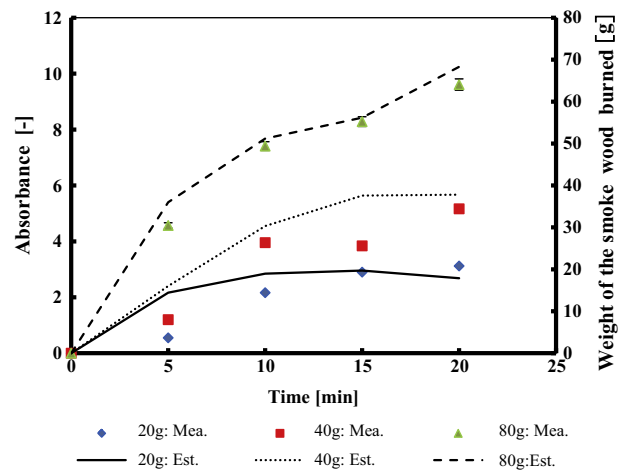


Fig. 7. Measured values of smoke components absorbed in water and estimated absorbance calculated using the weight of the smoke wood burned (Eq. (12)). Bars indicate standard deviation from 5 determinations.

the casing was responsible for the decreased migration to the surface of the ham (see values close to the surface of the casing in Fig. 6). Similar results were reported by Sanches-Silva et al. (2010) for the case of DPBD in pork meat.

### 3.3. Analysis of the migration of smoke components into ham based on the concentration in the smokehouse

#### 3.3.1. Estimation of $C_{We}$

In Fig. 7, the changes in the absorbance ( $A$ ) of the smoke components in water inside the smokehouse using 20, 40, and 80 g as the initial weights of smoke wood during 20 min of smoking are presented. The amount of burned smoke wood is also shown. When an initial value of 20 g of smoke wood was used, nearly all the smoke wood was burned in around 15 min. However, with more smoke wood, even after 20 min, some smoke wood remained in the smokehouse generator. Rostami et al. (2003) claimed that smoke proceeded at a constant speed in a model of a smoldering cigarette during gas-phase combustion. Since the cherry wood used in this study presented very few impurities, and the wood was immobilized during the heating process, the flow of smoke and combustion of smoke wood were considered to be constant for the calculations.

Fig. 7 includes the  $A$  of several phenol components besides the 2,6-dimethoxyphenol. These results were difficult to simulate, because the behavior of all phenol components of the smoke wood was difficult to follow. For this reason,  $C_{Wm}$ , which included a single peak for 2,6-dimethoxyphenol in the HPLC experiments, was used even though the results varied slightly compared to  $A$ . In addition, to avoid complicated experiments involved in HPLC determinations,  $C_{We}$  could be estimated by empirical equations. The experimental results for the  $C_{We}$  estimation are shown in Fig. 8.

The relationship between  $A$  and the weight of the smoke wood burned,  $W$ , ( $30 \leq W \leq 100$ ) for the 20 min smoking step is shown in Fig. 8A. A linear correlation was observed (coefficient of determination,  $R^2 = 0.996$ ).

$$A = 0.1354 * W \quad (10)$$

The relationship between  $A$  and  $C_W$  in the smokehouse is shown in Fig. 8B. A linear correlation was observed ( $R^2 = 0.995$ ).

$$C_W = 1.737 * A \quad (11)$$

where  $A$  was in the range of  $0.3 \leq A \leq 10$ . Finally, the  $C_W$  was correlated to the  $W$  in Fig. 8C. A linear dependence was observed and the coefficient of determination ( $R^2$ ) was 0.964.

$$C_{We} = 0.2432 * W \quad (12)$$

Thus, by measuring  $W$ , the estimation of  $C_{We}$  using Eq. (12) is possible without HPLC experiments, which are sometimes difficult and time-consuming. Ishikawa et al. (1975) and Oota et al. (1997) reported that smoke components dissolved in distilled water have a maximum absorption band in the ultraviolet region. Thus, even though the amount of smoke components dissolved in water and those in the smoking air are not the same, they can be combined to define the amount of  $C_{We}$  based on  $W$ , as demonstrated in this study. Combining Eqs. (12) and (13) (explained in the next section), facilitated the estimation of the profiles shown in Fig. 7, which agreed in all cases with the measured profiles.

#### 3.3.2. Migration of smoke components into ham

Based on the results shown in Fig. 6, the overall mass transfer coefficient ( $U = 1.03 \times 10^{-9} \text{ m s}^{-1}$ ) did not change within the same smoking conditions, regardless of the positions of the sample model. Thus, by varying  $C_{max}$  according to their respective  $C_W$ , the theoretical value can be approximated to the measured value of the concentration of the smoke index under any smoking

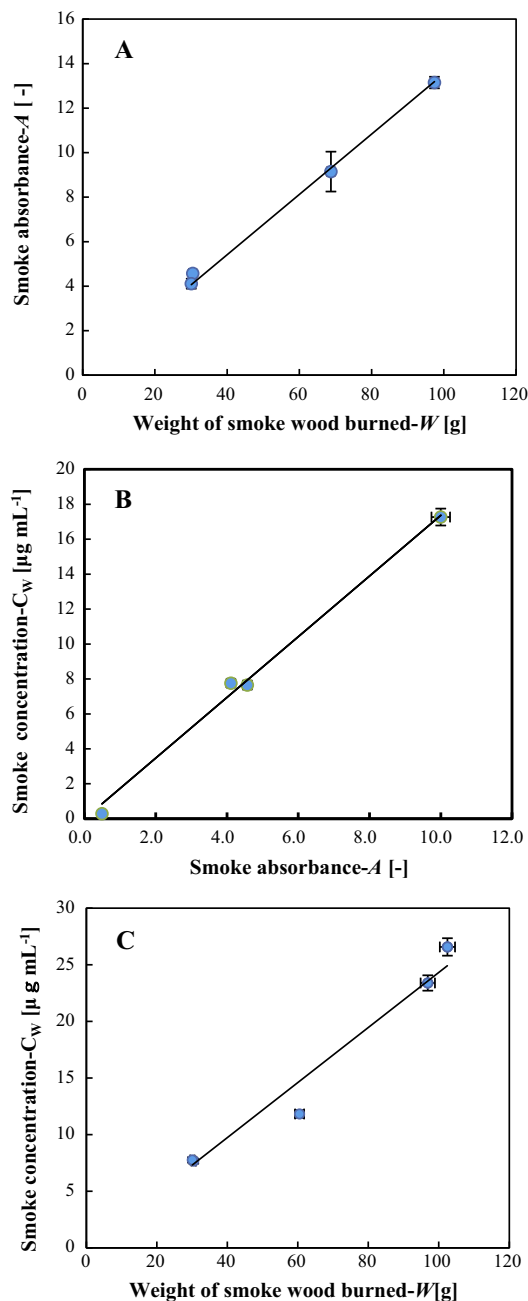


Fig. 8. Relationship between smoke component absorbance and weight of the smoke wood burned (A). The smoke component absorbance and smoke component concentration in the smokehouse (B). Weight of smoke wood burned and the concentration of smoke component in the smokehouse (C). Samples were smoked for 20 min. Bars indicate standard deviation from 5 determinations.

conditions. The values are shown in Table 3, and were calculated using Eq. (13):

$$C_{max} = C_{max\ st} * C_{We}/C_{Wst} \quad (13)$$

where  $C_{max\ st}$  is the hypothetical standard equilibrium absorption ( $153.5 \mu\text{g g}^{-1}$ ) obtained using 40 g of initial smoke wood,  $C_{Wst}$  is the concentration of smoke components in the smokehouse using 40 g of smoke wood ( $9.20 \mu\text{g mL}^{-1}$ ), and  $C_{We}$  is the concentration of smoke components in the smokehouse calculated from the weight of burned smoke wood using Eq. (12).

The measured and estimated smoke migrations, after a 20 min smoking step, are evaluated in Fig. 6 as a function of the

**Table 3**Parameters for the diffusion equation and the estimation of the smoke component concentration inside the smokehouse ( $C_{We}$ ).

| $C_{We} = 0.2432 * W$ ( $\mu\text{g mL}^{-1}$ )                                                                                  | 4.72                  | 9.20                  | 17.54                 |
|----------------------------------------------------------------------------------------------------------------------------------|-----------------------|-----------------------|-----------------------|
| Initial weight of the smoke wood (g)                                                                                             | 20.00                 | 40.00                 | 80.00                 |
| Weight of the smoke wood burned, $W$ (g)                                                                                         | 19.42                 | 37.82                 | 72.14                 |
| Amount of the hypothetical concentration equilibrium absorption at the surface of the casing, $C_{max}$ ( $\mu\text{g g}^{-1}$ ) | 78.77                 | 153.53                | 292.71                |
| Overall mass transfer coefficient, $U$ ( $\text{m s}^{-1}$ )                                                                     | $1.03 \times 10^{-9}$ | $1.03 \times 10^{-9}$ | $1.03 \times 10^{-9}$ |

concentration of the smoke components ( $C$ ) at different sampling positions in the radial direction from the core to the surface of the ham with different quantities of smoke wood. Experiments were conducted immediately after processing. The concentration of smoke components was greater at the surface than at the internal positions. Moreover, the  $C$  in the surface layer portion varied depending on the amount of smoke wood used; an initial amount of 20 g of smoke wood resulted in a lower  $C$  value. However,  $C$  did not penetrate to the core of the ham.

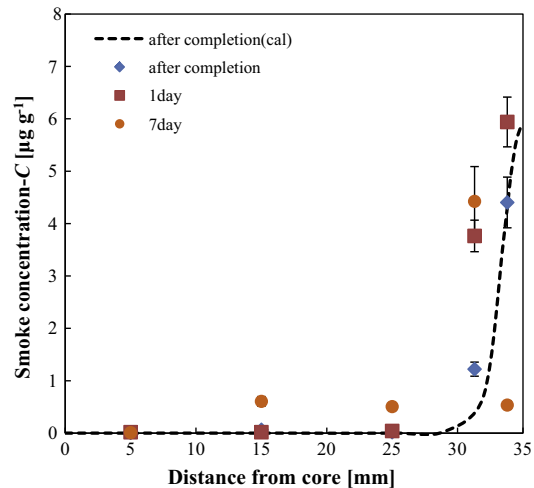
According to Miyahara et al. (1998), more than 90% of the phenol components in loin ham after smoking were found in the first 10 mm from the surface. Similar results were obtained in this study. Thus in each run, approximately 75% of the total  $C$  was found in the surface layer (32.5–35.0 mm) and 85% was observed between 30.0 and 35.0 mm. Therefore, the difference in the internal  $C$  could be explained by the  $C$  at the surface layer, which may be influenced by the moisture content. Similar results were reported by Oota et al. (1997). Notably, the  $C_w$ , as well as thermal schedule and moisture content at the ham surface, influenced the migration of smoke into ham.

The small differences between the estimated and measured values (Fig. 6) can be due to the measurement method, because the  $C$  value was measured at all radial positions in the considered range. Samples used to prepare 2 g of extract contained many locations, and therefore might explain the large standard deviation of the measured values. In addition, a homogeneous meat was assumed in the estimation of the migration results, which could introduce error. However, in spite of these factors, Eq. (13) facilitated the prediction of  $C$  values even for smoke processes using different weights of smoke wood with fair to good agreement with the measured values.

#### 3.4. Migration of smoke components into ham during storage

In Fig. 9, the measured values of  $C$  during storage are presented. The smoke components migrated into the ham slightly with increasing storage times; however, the diffusion did not proceed to the core. After one day, the smoke components migrated into the internal portion of the ham, more than in samples analyzed immediately after ham production. In particular, the  $C$  at the surface zone of 32.5–35.0 mm after one day was approximately 3 times that at 30.0–32.5 mm, and 1.5 times that immediately after production. After 7 days of storage, the  $C$  was greater than other evaluation periods for all evaluated positions, with the exception of the position closer to the surface, which was less than that in other evaluation periods. These results confirmed that the smoke components migrated from the surface of the casing at a slow rate during storage. According to Herring and Smith (2012) and Sanches-Silva et al. (2007), the migration of smoke components at low temperatures is reduced. As samples were stored at 4 °C, the progressive migration inside the ham may have been affected. Sanches-Silva et al. (2010) reported five times more migration of DPBD into pork meat at 70 °C than at 5 °C.

Moreover, a drip from the ham was observed, explaining why the amount of smoke components near the surface of the ham decreased. With smoked beef, Oota et al. (1997) suggested that



**Fig. 9.** Measured and estimated concentration of smoke components in pork loin ham during storage (40 g of initial smoke wood was used). Bars indicate standard deviation from 5 determinations.

the decomposition of phenol occurred during storage, thus decreasing its content at the surface. This could explain why the total amount of smoke index observed during storage was low in this study. The degradation of smoke index inside the smoked product, and volatilization of volatile components, such as elimination by dripping, were relevant in this study and further investigations are required.

#### 4. Conclusions

Smoke processing is a traditional preservation technology that combines the effects of salting, deposition of smoke components, and drying. However, the migration of smoke components has not received adequate attention. In this study, we analyzed the migration of smoke components into ham, using the differences in the concentration of smoke components in the smokehouse ( $C_w$ ) during processing.

2,6-Dimethoxyphenol was used as a smoke index. Mass transfer and diffusion coefficients were obtained to estimate the smoke migration. A significant contribution of the transfer coefficient for the surface of the ham from the casing,  $\beta$ , was responsible for the low migration to the surface of the ham. A linear correlation between the  $C_{We}$  and the weight of burned smoke wood was obtained.  $C_{We}$  values were used to estimate the  $C_{max}$  for different smoking conditions, which permitted the estimation of the concentration of smoke components ( $C$ ) at several internal positions of the ham. The estimated  $C$  values agreed well with measured values, independent of the initial weight of smoke wood used in the smoking step. Finally, the analysis confirmed the migration of smoke from the surface of the casing, where the smoke components were deposited during the smoking step, to the interior without reaching the core after 7 days of storage.



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