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MODELLING OF SIMULTANEOUS TRANSPORT OF HEAT, MOISTURE, AND SODIUM, CHLORIDE AND HYDROGEN IONS DURING MEAT EMULSION COOKING

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INTRODUCTION

With the growing importance on industrial and institutional food preparation, heat and mass transfer data is necessary for the development of optimal cooking procedures, equipment and installations. Carefully controlled thermal processes are necessary to develop the initial colour, characteristic skin and internal texture, and eliminate trichinella and microbial population without emulsion destabilization, excessive moisture loss or texture changes. The preservation of meat by salt depends on salt reaching all parts of the meat, including the fatty tissues. The pH of meat is important because it affects meat colour, bacterial growth, and water holding capacity (WHC).

A few studies have been undertaken to describe the transport of heat, moisture and various ions. Monagle et al. (1974) determined experimentally the effect of temperature, humidity and air velocity on weight changes and temperature profiles in frankfurters during thermal processing. However, no mathematical models were developed. Mittal and Blaisdell (1983) developed a simplified two term model to predict the weight loss of frankfurters during thermal processing at various process conditions and product compositions. Mittal and Blaisdell (1982a) developed simultaneous heat and mass transfer model with Fickian type diffusion to predict the temperature and moisture profiles in frankfurter during cooking.

The moisture and salt flow and distribution within a sausage product, Danish Salami, was investigated by Fruelund (1970) during thermal processing. He, however, simplified the model by ignoring salt flow due to the movement of water. The temperature effect was also neglected. Mittal and Blaisdell (1982b) developed a simulation model to predict the distribution of sodium and chloride ions' concentrations by considering diffusion and convection. Mittal and Blaisdell (1982c) also developed a simulation model by considering diffusion, convection and first order chemical reaction to predict the hydrogen ion profiles during cooking of frankfurters.

This paper presents a determination of the temperature, moisture, and sodium, chloride and hydrogen ions distribution in meat emulsion sausage of cylindrical geometry at several process times as a function of composition, process temperature and relative humidity, with models for determining the corresponding moisture, heat and ions mobility.

MATERIALS AND METHODS

A central composite rotatable design was employed for the experiments (Cochran and Cox 1957). For three factors this design consisted of 20 experiments i.e. 8 vertices of a cube (2^3 factorial), 6 centre points for replication and 6 star points to give the design the property of being rotatable. Since heat, mass and ions transport parameters follow Arrhenius relationship, the linear coordinate for temperature was chosen as the inverse of absolute temperature. Similarly, the linear coordinates for FP and RH were their logarithmic values. Table 1 presents the variables and their actual levels obtained after transforming them for these investigations. The order of experiments was completely randomized.

Fresh emulsion was prepared before starting each experiment in the laboratory in a modified Waring Blender (Mittal 1979). The formulation included nonfat dry milk (3%), salt (2.5%), sucrose (0.5%), corn syrup solids (2%), spices and curing agents. Protein, fat and water were added according to the desired fat protein ratio (FP). Most of the fat was taken from the pork meat and protein from the lean beef. The viscosity of the emulsion was used as an index of the extent of chop.

A closed loop wind tunnel was used to provide the controlled environment (Figure 1). The wind tunnel consisted of a fan, heating and cooling sections, steam injection system, drying column and a test section. The temperature was controlled by proportional rate and integral modes to within $\pm 1^{\circ}C$. The humidity was controlled to within $\pm 1\%$ by injecting steam and venting the circulating air. The airflow was controlled within ± 0.01 m/s with an orifice, a pressure transmitter and a flow recorder-controller to regulate a butter fly valve.

Meat emulsion was stuffed into polyethylene casing of 2.5 cm diameter with the help of a hand stuffer. Various identical frankfurters of about 15.2 cm length and of same weight were suspended in the test section with a frame of galvanized wires. Into one frankfurter, four copper-constantan thermocouple probes were inserted axially at different locations. The probes were extended 7.6 cm through a plastic stopper which was inserted at the top of the casing as a thermocouple position guide. To prevent moisture losses from the sides of plastic stopper, the sides and holes were coated with a high vacuum grease. One of the frankfurters was used to record weight at intervals. The processing was stopped when product had lost about 13% of the initial weight. The equilibrium moisture contents of the meat emulsion were recorded for different processing conditions and formulations. The emulsion was spread in thin aluminum foil discs for this purpose. Four other frankfurters wee used for the determination of moisture profiles and associated dimensional changes during the different stages of cooking. These moisture profiles were measured at about 4,7,10 and 13% moisture losses.

After the loss of desired moisture, the entire frankfurter was chilled immediately into the acetone dry ice solution for quick freezing. The acetone dry ice solution was maintained below $-45^{\circ}C$ in a Cryocool cooler. A frozen disk from the central 2 cm was then divided into ten thin radial sections with stainless steel cork borers of different diameters. The moisture contents of these thin rings were then determined by oven method. The moisture profile was developed by assigning the mean moisture content (dry basis) to the mean location on the respective slice.

Sodium, chloride and hydrogen ions sensitive micro-electrodes were inserted in separate frankfurters. Four ion sensitive and one reference micro-electrode for sodium and chloride ions, and five ion sensitive and two reference micro-electrodes for hydrogen ion were inserted in the frankfurter from one end. The output of the microelectrodes were recorded continuously on a millivolt recorder after one minute interval. These micro-electrodes were calibrated before insertion at 30,50 and $70^{\circ}C$ and at several concentrations of ions.

MATHEMATICAL MODELLING

The following assumptions were made to define the process mathematically.

1. An infinitely long ($L/(2D) > 5.5$), and homogeneous cylinder.
2. Uniform initial temperature, moisture and ions distribution.
3. Constant thermal properties of emulsion.
4. Ambient air temperature and humidity ratio to be a step function of time.
5. An infinite mass transfer coefficient at the surface. The mass transfer Biot number >>10; the air velocity was 1.7 m/s in the test section for this purpose.
6. Negligible shrinkage: The changes in length were 0 to 5%, and the changes in diameter were +5%.

7. Since the concentrations of ions were small, the ions diffusivity and reaction rate constant were considered independent of concentration.

Temperature and Moisture

A transport mechanism of liquid diffusion followed by a vaporization at the surface was considered. Based on above mentioned assumptions, the mathematical model characterizing simultaneous heat and mass transfer can be represented as:

$$\frac{\delta m}{\delta t} = \frac{1}{r}\frac{\delta}{\delta r}\left(D_m \cdot r\,\frac{\delta m}{\delta r}\right) \qquad (1)$$

$$\frac{\delta T}{\delta t} = \alpha\left(\frac{\delta^2 T}{\delta r^2} + \frac{1}{r}\frac{\delta T}{\delta r}\right) \qquad (2)$$

Initial Conditions: $T(0,r) = T_o,\ m(0,r) = m_o$ (3)

Boundary Conditions: At $r = 0,\ \frac{\delta T}{\delta r} = 0,\ \frac{\delta m}{\delta r} = 0$

$$\text{At } r = R,\ \frac{\delta T}{\delta r} = \frac{-h_T}{k_h}(T_s - T_a) + \frac{D_{m,10}\rho_D}{k_h} \cdot L_v \cdot \frac{\delta m}{\delta r} \qquad (4)$$

$$m(R,t) = m_e$$

Where $D_{m,10}$ is the mass diffusivity at the surface node. Other symbols are defined at the end of the paper.

Taking as nondimensional variables:

$$C = (m-m_e)/(m_o-m_e),\quad \theta = (T-T_o)/(T_a-T_o) \qquad (5)$$

$$\psi = r/R,\quad Bi_H = h_T R/k_h \qquad (6)$$

$$\lambda_1 = D_{m,10}\rho_D\ L_v\ (m_o-m_e)/(k_h(T_a-T_o)) \qquad (7)$$

Substituting (5) to (7) in eq. 1 to 6

$$\frac{\delta\theta}{\delta t} = \frac{\alpha}{R^2}\left(\frac{\delta^2\theta}{\delta\psi^2} + \frac{1}{\psi}\frac{\delta\theta}{\delta\psi}\right) \qquad (8)$$

$$\frac{\delta C}{\delta t} = \frac{1}{R^2}\left[\frac{\delta D_m}{\delta\psi} \cdot \frac{\delta C}{\delta\psi} + \frac{D_m}{\psi}\frac{\delta C}{\delta\psi} + D_m\frac{\delta^2 C}{\delta\psi^2}\right] \qquad (9)$$

$$\theta(0,\psi) = 0,\quad C(1,t) = 0 \qquad (10)$$

$$\text{At } \psi = 0,\quad \delta\theta/\delta\psi = 0,\quad \delta C/\delta\psi = 0 \qquad (11)$$

$$\text{At } \psi = 1,\quad \delta\theta/\delta\psi = -Bi_H\,(\theta_{\psi=1} - \theta_a) + \lambda_1\,\delta C/\delta\psi \qquad (12)$$

Sodium and chloride ions

The transport of these ions takes place as diffusion in the liquid phase and by convection due to moisture mobility.

$$\text{Diffusion} = -DI \cdot d\,CI/dr \cdot 2\pi rL \cdot CW \cdot \rho_m \cdot 1000/\rho_w \qquad (13)$$

$$\text{Convection} = CI \cdot D_m \cdot dC/dr \cdot 2\pi rL \cdot CW \cdot \rho_m \cdot 1000/\rho_w \qquad (14)$$

$$\text{Accumulation} = d\,CI/dt \cdot 2\pi rL \cdot \Delta r \cdot 1000 \qquad (15)$$

A general form of mass balance equation used is:

Rate of mass in - Rate of mass out = Rate of mass accumulation

The cylinder was divided into ten concentric sections and the concentration of ions was assigned to the centre of each node. The rate of change of concentration of ions with time at various nodes was calculated using eq. 13 to 15 and the following initial and boundary conditions:

$$CI(r,0) = CI_o, \quad dCI/dr\ (R,t) = 0, \quad dCI/dr\ (0,t) = 0 \qquad (16)$$

Hydrogen ions

The net mobility of hydrogen ions is considered due to the solvent diffusion in liquid phase, the convection due to moisture transport, and the depletion due to chemical reaction of first order. For these mechanisms, the following equations were developed.

$$\text{Diffusion} = -DIH\ .\ A.\ dCIH/dr \qquad (17)$$

$$\text{Convection} = CIH\ .\ D_m\ .\ A\ .\ dC/dr \qquad (18)$$

$$\text{Rate of depletion} = -KR\ (CIH - CIH_e)\ .\ V \qquad (19)$$

$$\text{Accumulation} = dCIH/dt\ .\ V \qquad (20)$$

Again the cylinder was divided into ten radial sections. Based on the conservation of mass principle, the equations were developed for the change of hydrogen ion concentration with time at various nodes.

To solve the model with digital computer employing the Continuous System Modelling Program (CSMP) the sapce cordinate (eq. 8 to 12) was eliminated as a variable by dividing the cylinder into ten concentric shells. The moisture and temperature ratio profiles within each shell were approximated by a parobola (Hamdy and Barre 1969). The derivative of moisture diffusivity with respect to distance was solved by a backward difference method.

To analyze moisture profiles, the moisture diffusivity was considered to be a function of product temperature and moisture concentration. The following Arrhenius model was considered appropriate:

$$D_m = \text{Exp}\ (-A_1 + A_2/T_{abs} + A_3C) \qquad (21)$$

Equilibrium moisture content

Equilibrium moisture contents of the meat emulsion at various conditions and compositions were recorded. The Chung and Pfost (1967) equation with a term of FP gave the best fit. The following model was obtained giving a coefficient of determination (r^2) of 0.965.

$$m_e = -0.102\ \ell n \left[-Rg.FP(T + 5.665)\ \ell n\ (RH)/1.132E7\right] \qquad (22)$$

RESULTS AND DISCUSSION

Moisture Profile

Figure 2 shows the nondimensional moisture ratio history at different nodes. The moisture profiles are very steep and large moisture gradients exist near the surface. Migration of solutes primarily due to the bulk flow of the solvent to the surface of frankfurter might also be associated with case hardening. The concentration of moisture at the centre of frankfurter has changed little even after the removal of about 13% moisture (wet basis). The slopes of these curves are decreasing with time.

Moisture Diffusivity

The model of simultaneous heat and mass transfer was used to predict moisture and temperature profiles. The complete model of moisture diffusivity is given by:

$$D_m = \text{Exp}\left[8.6787 + 0.1348\ FP - 4341.5/T_{abs} + 8.55\ C\right] \qquad (23)$$

The values of diffusivity are decreasing with the increase in moisture ratio exponentially. These diffusivity values are increasing with the increase in temperature, which is in accordance with the Arrhenius relationship.

Temperature Ratio Profile

Figure 3 illustrates the observed and predicted temperature ratios at four locations in a frankfurter during cooking at the central point of the design. The temperatures at all locations increase at a rate of about 1.5°C/min in the beginning. After a steep rise, the temperatures increased very little to a level above wet bulb temperature. There was negligible temperature gradient inside the frankfurter after the steep rise in temperature.

Sodium and Chloride Ions Profiles

Figure 4 illustrates the predicted and observed values of $C\ell^-$ concentrations for one test conditions. These show that there is a good agreement between predicted and observed values. Similar results were obtained for Na^+ concentration profiles and for other experimental conditions.

The figure 4 indicates that the concentrations of Na^+ and $C\ell^-$ are decreasing initially for about 15 min at the node 11 mm from the centre of the frankfurter. After that the concentrations are increasing rapidly, and asymptotically approaching a nearly constant value as the surface reaches a moisture equilibrium, and diffusive movement and association with product components balance the convective input. The concentrations of the ion at about 7.9 mm from the centre of the frankfurter decreased initially and then increased exponentially with time. The initial gradient of water is relatively large and a large volume of ions is being transported to the surface by convection from adjoining regions. The ion gradients have not been established at this stage and the diffusion of ion is contributing little.

At lesser distance such as 4.7 mm from the centre of the frankfurter, the concentrations remain constant for about 15 to 25 min and then decrease. After a considerable time, the concentrations are nearly constant. At the centre of the frankfurter, the concentrations are not changing initially. After that, the concentrations decrease steadily during the test due to lateral diffusion and convection.

Ions Diffusivity

The diffusion coefficient values of Na^+ varies between 5.03 E-6 and 7.83 E-6. The diffusivity values are increasing with an increase in temperature. Similarly, the $C\ell^-$ diffusion coefficients vary from 5.31 E-6 to 8.50 E-6 m^2/h for similar conditions. Based on the Eyring's Absolute Reaction Rate Theory, the following models were developed:

$$DIN = 0.901\ T_{abs}\ .\ Exp\left[-0.099\ FP - 1264/T_{abs}\right], \quad r^2 = 0.998 \qquad (24)$$

$$DIC = 0.852\ T_{abs}\ .\ Exp\left[-0.068\ FP - 1244/T_{abs}\right], \quad r^2 = 0.996 \qquad (25)$$

Hydrogen Ion Profiles

Figure 5 illustrates the H^+ concentration changes with time at various locations in the frankfurter. It is clear that the concentrations are decreasing at all the locations with time. At the start of cooking there is a sharp decrease of concentration, and at the end of cooking these curves are indicating an apparent equilibrium pH value. The following model for equilibrum H^+ concentratio

was obtained giving r^2 value of 0.99:

$$pH_e = 0.0113\ T_{abs}\ .\ Exp\left[(4.131\ E\text{-}3 + 2.329\ E\text{-}3\ RH)\ FP + 148.9/T_{abs}\right] \qquad (26)$$

An increase of 0.27 to 0.50 pH units was noted in these experiments. The minimum increase was at 58°C and maximum was at 76°C. Figure 5 illustrates the predicted and experimental values of the H^+ concentrations at various locations in the frankfurter. Deviations in the order of 0.015 pH unit or less are visible.

Hydrogen Ion Diffusivity and Reaction Rate Constant

The values of the H^+ diffusivity were found to be constant at 0.2 E-5 m^2/h for various conditions.

The values of the first order reaction rate constant (KR) for various processing conditions and compositions of the product vary between 0.88 and 2.90 h^{-1}. The KR is increasing with the increase in temperature. Based on the Eyring's Absolute Reaction Rate Theory, the following model was fitted for KR giving r^2 value of 0.96:

$$KR = 785.11\ T_{abs}\ .\ Exp\ (-0.133\ FP - 3935/T_{abs}) \qquad (17)$$

CONCLUSIONS

1. Simultaneous heat, moisture, and sodium, chloride and hydrogen ions transfer models predict the temperature, moisture and ions profiles in the product during cooking satisfactorily.
2. The moisture profiles are very steep and large moisture gradients exist near the surface of the frankfurter and are associated with the surface skin formation. There is a negligible temperature gradient inside the frankfurter after the steep rise in temperature.
3. The diffusion coefficient of Na^+ varies between 5.03 E-6 and 7.83 E-6 m^2/h, and for $C\ell^-$ from 5.31 E-6 to 8.50 E-6 m^2/h for product temperatures between 58°C and 81°C.
4. An increase of 0.27 to 0.50 pH units was recorded in the processed product. The values of reaction rate constant varies between 0.88 to 2.90 h^{-1}, and the diffusivity of H^+ was constant at 0.2 E-5 m^2/h.
5. The diffusivities are functions of concentration, composition and temperature of the product.
6. The models developed considering diffusion, convection and first order reaction was able to predict H^+ concentration reasonably well.

LIST OF SYMBOLS

A	frankfurter cross sectional area, m^2
Bi_H	Biot modulus of heat transfer, h/K
C	concentration of water, dimensionless
CI	ions concentration, mol/ℓ
CIH	H^+ concentration, mol/ℓ
CW	water content, decimal wet basis
D	diameter of frankfurter, m
DI	ions diffusivity, m^2/h
DIC	chloride ion diffusivity, m^2/h
DIH	diffusivity of H^+, m^2/h
DIN	sodium ion diffusivity, m^2/h
D_m	diffusivity of water, m^2/h
FP	fat-protein ratio
h_T	heat transfer coefficient, $kJ/(h.m^2.K)$
KR	reaction rate constant, 1/h
k_h	thermal conductivity, kJ/(h.m.K)
L	frankfurter length, m
L_v	latent heat of vaporization of water, kJ/kg
m	moisture content, decimal dry basis
R	radius of frankfurter, m
RH	relative humidity, decimal
Rg	gas constant, kJ/(kg.K)
r	radial distance, m
r^2	coefficient of determination
T	temperature, ^oC
t	time, h
V	volume of a frankfurter section, m^3
α	thermal diffusivity, m^2/h
ρ_D	density of dry matter, kg/m^3
ρ_m	density of the mixture of ingredients, kg/m^3
ρ_w	density of water, kg/m^3
ψ	nondimensional distance, r/R
λ_1	dimensionless ratio of latent heat to sensible heat
θ	temperature ratio

Subscript

a	air
abs	absolute
e	equilibrium
o	initial
s	surface

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Table 1. Variables and their levels for experiments

Variable	Variable levels				
	-1.68	-1.0	0.0	1.0	1.68
Temperature (°C)	58	63	69	76	81
Relative humidity (%)	41	48	60	75	87
Fat-protein ratio	1.2	1.4	1.9	2.5	3.0

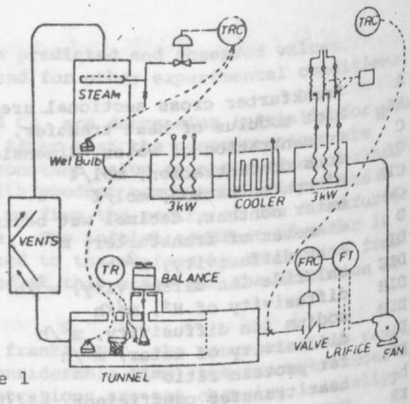

Figure 1

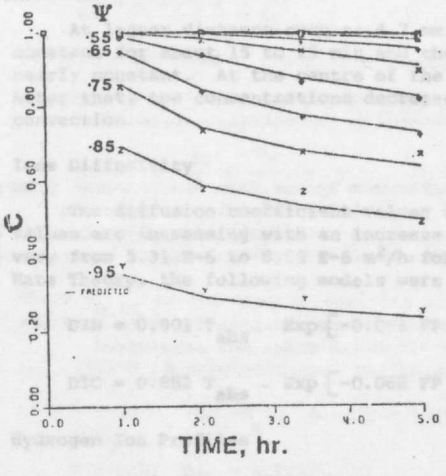

Figure 3

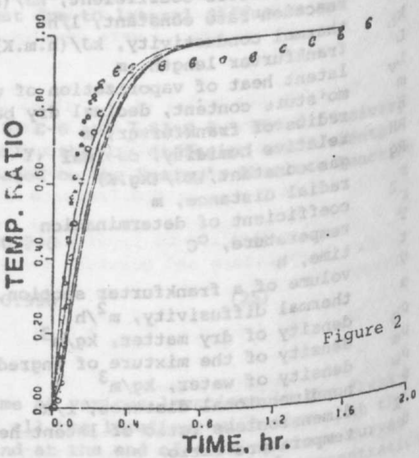

Figure 2

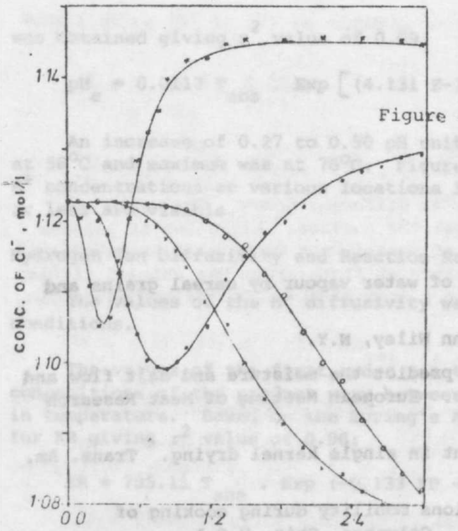

Figure 4

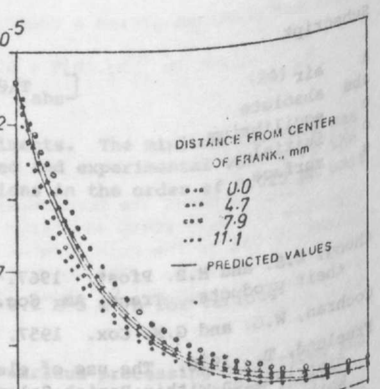

Figure 5

Figure 1: Flow diagram of experimental setup.

Figure 2: Experimental and predicted moisture ratios at different locations in frankfurter of 1.9 FP during cooking at 58°C and 68% RH.

Figure 3: Predicted and experimental temperature ratios in frankfurter of 1.9 FP during cooking at 81°C and 60% RH. ψ = 0.0, 0.4, 0.6 and 0.9 for lower to upper curves, respectively.

Figure 4: Predicted and observed chloride ion profiles, at different locations in frankfurter of 1.9 FP, during cooking at 69°C and 60% RH. -: Predicted, 0:0.0, x:4.7, •:7.9, and *:11.1 mm from the centre of frankfurter.

Figure 5: Distribution of H^+ concentration during cooking of frankfurter at 58°C, 60% RH and 1.9 FP