Causes and Prevention of Weight Losses in Frozen Fishery Products during Freezing and Cold Storage

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INTRODUCTION

A major problem encountered during the freezing of fishery products and subsequent frozen storage is desiccation, which is the loss of moisture by a product to its surroundings, thus producing a weight loss in the product. An excellent example is found in the production and distribution of frozen, breaded shrimp.

The Standard of Identity for breaded shrimp (Section 36.30 (b) of 21 CFR) specifies that breaded shrimp that are produced and marketed in the United States must contain not less than 50% shrimp. However, when shrimp are battered, breaded, packaged, and placed in frozen storage, several physical and chemical changes occur, one of which is the migration of water molecules from the shrimp to the breading material. Water molecules migrate from the shrimp to the breading material because of many factors, including the fact that the breading material has a lower percent moisture than the shrimp meat. Such factors that allow water to migrate from the shrimp to the breading material result in dehydration loss of weight in the shrimp component of the breaded product.

To enforce the Standard of Identity, the Food and Drug Administration regulatory personnel conduct periodic inspections of breaded shrimp. If a shipment is found to contain more than 50% breading material, the product is deemed to be in violation of the Standard of Identity, and is usually removed from the market, regardless of its composition at the time of packaging. The contention of the Food and Drug Administration is that because the breading material is normally cheaper than the shrimp, there is a tendency for the processor to over-bread his product. Seizure of the product and the time involved in litigation deprive the processor of marketing opportunities and result in heavy and unnecessary financial losses.

Weight losses in frozen fishery products may be divided into three categories:(1) mechanical losses, (2) damage or down-grading of products, and (3) dehydration. For both of the first two categories the causes of the losses are usually simple to establish and depend entirely on factory conditions. It is primarily the losses caused by dehydration that require closer study.

THEORY OF DEHYDRATION

The major problem encountered when freezing fishery products and in their sequential frozen storage is desiccation. Desiccation is the loss of moisture by a product to its surroundings thus producing a negative weight change in the product. This loss of moisture occurs by one or both of the following mechanisms: (1) evaporation of water from the product's surface before it is frozen, and (2) sublimation of ice from the product once it is frozen.

There are several factors that determine the amount of evaporative loss a product will undergo. The thicker the product, the more moisture is evaporated. Thickness affects the length of time necessary to freeze, therefore directly affecting the length of time that evaporative loss can occur (14). If a product is frozen quickly, it will lose less moisture due to evaporation than if it were frozen slowly (16,14). The lower the temperature of the freezer and that of the product as it enters the freezer the less evaporative loss. Temperature affects the relative humidity, which is percent saturation, of the air in the freezer. Air loses its capacity to hold water as the temperature is lowered, thus lowering its ability to accept moisture from a product (12, 9). Temperature of a product is directly related to the vapor pressure exerted by the water it contains. Evaporative loss will occur at a rate dependent upon the difference between the equilibrium water vapor pressure of the product and the partial pressure of the water vapor in the air (1, Fig. 1). This loss will continue until the water vapor pressure of the product is equal to the partial pressure of the water vapor in the air or until the product is frozen (16, 9, 11).

Sublimation is the mechanism by which a substance changes from the solid phase to the gaseous phase without the appearance of the liquid phase. Ice will sublime if the vapor pressure it exerts is greater than the partial pressure of the water vapor in the air (11, 9, 1). Regulation of the relative humidity can be used to minimize the rate of sublimation. This can be done by enlarging the surface area of the cooling coils in the storage room. By enlarging the cooling coil's surface area, the difference in temperature between the storage room air and the cooling coils is decreased. The lessening of this difference in temperature increases the relative humidity and as a result retards sublimation (10, 2). This reduced temperature difference between the storage room air and cooling coils also reduces the amount of temperature fluctuation in the cold room and thus decreases the rate of sublimation (7). A product can be protected from sublimation by the use of a glaze. Glazing is the addition of a layer of ice around the product. The glaze doesn't stop sublimation but rather the glaze sublimes and is lost instead of the ice from the product's moisture (16, 10, 7).

Evaporation and sublimation can be minimized by eliminating voids and intermediate spaces in the package (18). The storage temperature should be kept constant (7). Air in the storage room should have its relative humidity adjusted so as not to allow it to pick up moisture from the product (10, 2). The package should be relatively impermeable to moisture, sealed tightly, and adhere to the product. (18, 6, 7, 3).

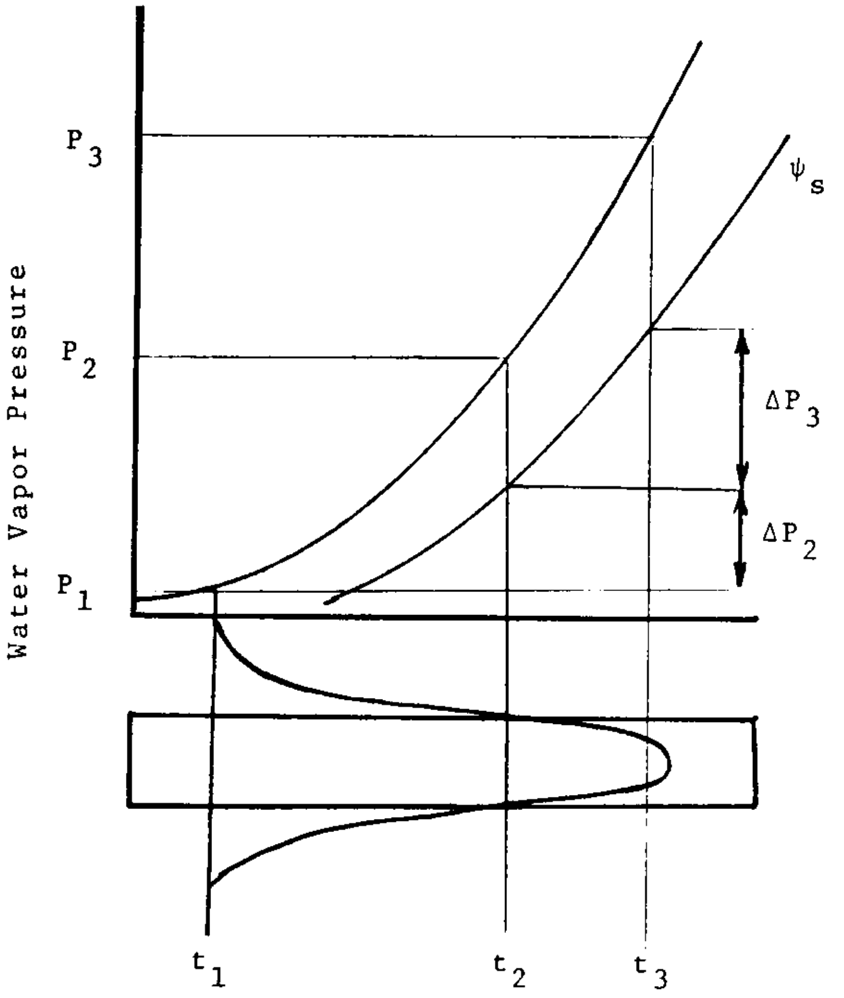


Fig. 1. Difference in water vapor pressure between the surroundings and a moisture containing substance(t_1 = Ambient temperature, t_2 = Surface temperature, t_3 = Average core temperature, and ψs = Water vapor pressure of the product).

MATERIALS AND METHODS

This investigation was undertaken in order to study the effects of four selected variables on the extent of moisture migrating within frozen breaded shrimp. The migration takes place from the shrimp meat into its coating of breading material. Two treatment levels for each of three variables were chosen for the study. These variables were (1) fine and coarse texture of breading material, (2) 40°F and 82°F as the temperatures at which the batter and breading were applied to the shrimp, and (3) slow and fast rates of freezing the breaded shrimp (slow taking about 4 h; fast taking about 3 to 4 sec). Together with these variables were five periods of elapsed storage time–1, 2, 3, 4, and 5 weeks–during which the frozen breaded product was kept at -6°F. These levels of texture, temperature, freezing rate, and periods of storage time yielded 40 different groups of frozen breaded shrimp. Since all the operations for each group were performed on five shrimp individually, a total of 200 randomly selected shrimp were prepared and used in studying the effects of the four variables on (1) the weight losses of shrimp meat during frozen storage, and (2) the concomitant weight gains of the breading coatings of these frozen shrimp. The two sets of gravimetric data, i.e. weight-loss of shrimp meat and weight-gain of breading coating, and two corresponding sets of percentage values based on initial weights of shrimp and breading material, each represented measurements that correspond to those of a 2 x 2 x 2 x 5 factorial arrangement of treatments in a randomized block design with five replicates. Each of these four sets of data was subjected to standard analysis of variance.

Sources of Raw Materials

A 20-lb lot of 40-count size, unpeeled, headed, freshly-frozen shrimp[1] (*Penaeus setiferous*) was received by air freight from Tampa, Florida. Prior to use in the present study, the shrimp were stored no longer than 2 weeks in the cold storage room in the Department of Food Science, LSU, at -6°F. Commercial breading materials, consisting of one 50-lb bag of batter mix[2] and two 50-lb bags of breading[2] (one of fine texture, the other coarse) with the ingredient composition of the two being the same, were obtained for preparing the coating of breading material that was applied to the shrimp.

Preparation of Breaded Shrimp

About 10 lb of the frozen shrimp were removed from the cold room and thawed by immersion in tap water. After being thawed, the shrimp were immediately shelled with removal of the terminal segment, deveined, washed in cold water, and placed in a bed of crushed ice to insure no change in quality. After approximately 400 shrimp had been peeled, deveined, and washed, a total of 100 shrimp for the slow freezing operation were removed, one at a time at random, from the crushed ice. These were then blotted with absorbent paper to remove excess adhering moisture and weighed. The weighing was done in order to determine the proper amount of breading material necessary in the coating to yield a breaded product that consisted of 50% shrimp and 50% breading material.

The batter had been prepared by mixing two parts batter mix with three parts water and allowing it to come to the proper temperature. Each shrimp, after being weighed, was immediately coated with batter and then dipped into the breading material until the weight of the coating was equal to that of the shrimp.

[1]Supplied by Treasure Island Seafood Company, Tampa, Florida

[2]Supplied by Modern Maid Food Products, Inc., Pontchatoula, Louisiana

The resulting individually prepared 50%–50% breaded shrimp was placed in a tared, appropriately identified sample bag of Nasco Whirl-Paks material. These particular bags were used because of their impermeability to gasses and moisture.

For the slow freezing operation, each individual bag containing a single breaded shrimp was placed in the freezer at -6°F immediately after the bag was sealed.

For the fast freezing operation, a total of 100 randomly selected specimens from a second batch of about 400 peeled, deveined, and washed shrimp were battered and breaded in the same manner as described above. Before being placed in its appropriately coded Nasco Whirl-Paks bag, each individually weighed 50%-50% breaded shrimp was immersed by means of tongs for 3 or 4 sec in liquid nitrogen contained in a Dewar flask. The fast frozen breaded shrimp was then bagged and immediately placed in the freezer at -6°F. Preliminary experiments had shown that if the shrimp were immersed in liquid nitrogen for longer than 4 sec, the texture of the shrimp was damaged and an inferior product resulted.

Gravimetric Measurements

The resulting eight treatment-groups (2 texture x 2 temperature x 2 freezing rate) of breaded shrimp that were stored at -6°F for sampling at weekly intervals were:

GROUP NUMBER	BREADING MATERIAL TEXTURE	TEMP. (°F)	FREEZING RATE
1	Fine	82	Slow
2	Fine	40	Slow
3	Coarse	82	Slow
4	Coarse	40	Slow
5	Fine	82	Fast
6	Fine	40	Fast
7	Coarse	82	Fast
8	Coarse	40	Fast

At the end of each of the five frozen storage periods–1, 2, 3, 4, and 5 weeks–five shrimp from each of the above eight groups, or a total of 40 specimens weekly, were removed from the freezer. Each of the 40 bags containing a single frozen breaded shrimp was weighed immediately upon removal from the freezer, after which the breaded specimen was removed from its bag, placed in a tared aluminum weighing pan, and weighed to the nearest 0.1 gram. While still in a frozen condition, the breading material was then dislodged from the shrimp with a stainless steel spatula, transferred to another tared weighing pan, and weighed. The weight of the frozen breading material and that of the shrimp were recorded. The pans containing the dislodged breading material, as well as those containing the shrimp meat, were placed in a drying oven at 120°C at atmospheric pressure and dried for 24 h or until the samples attained constant weight. The pans and contents were then removed from the oven, placed in a desiccator, allowed to cool, and weighed to the nearest 0.1 gram. The dry matter content of the shrimp and of the breading material were then computed from the gravimetric measurements.

RESULTS AND DISCUSSION

Mathematical Explanation

Breaded shrimp are cooled or heated by two mechanisms of heat transfer: convection and conduction. Cooling occurs when the product temperature is above the cold storage temperature and heating occurs when the product temperature is below the cold storage temperature. Convection transfers heat to and from the product's surface, thus setting up a temperature difference between the product's surface and its center. Conduction allows the transfer of heat within the product so as to destroy the temperature difference between the product's surface and its center.

Due to a temperature gradient within the product and a temperature difference between the product's surface and surroundings, various mechanisms of mass transfer occur. The controlling mechanism of mass transfer at a particular point in time depends upon the temperature profile of the product with respect to the temperature of the surroundings. Thus, it is obvious that the temperature profile of the product must be calculated with respect to time.

Certain assumptions must be made in order to facilitate the solution of the heat transfer equations involved. A constant geometric shape must be assumed (Fig. 2): (1) flat-slab, if the product is the butterfly type; (2) cylindrical, if the product is the round-breaded type. End effects and resistance to heat transfer at the shrimp-breading and breading-air interfaces will be assumed negligible. Round-breaded shrimp with the tails removed were used in this mathematical treatment.

The solution for the temperature history of the shrimp component must satisfy Fourier's Field Equations.

$$\frac{\partial T}{\partial t} = \alpha \nabla^2 T \quad \textbf{(I)}$$

where:

T = temperature, °F

∇ = differential vector operator

t = time, h

$\alpha = k/\rho C_p$ = thermal diffusivity, Ft^2/h

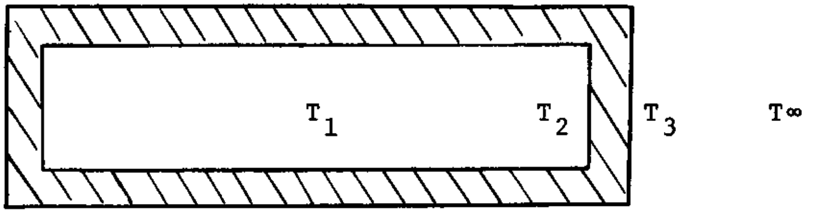
ρ = density, lb/Ft^3

k = thermal conductivity, BTU/n · Ft · °F

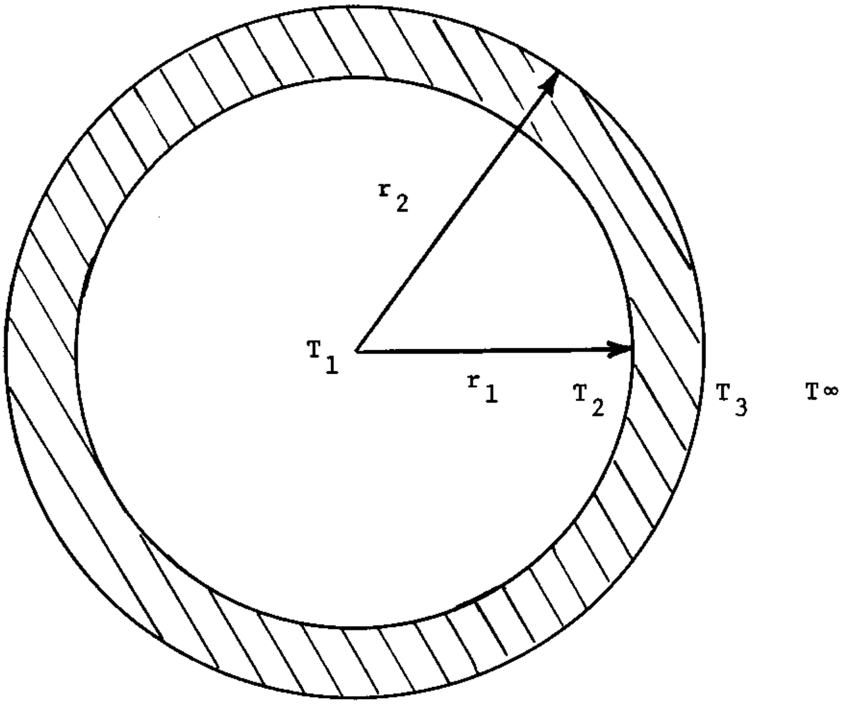
C_p = heat capacity, BTU/lb · °F

for cylindrical, coordinated, and negligible surface resistance equation I becomes:

$$\frac{\partial T}{\partial t} = \alpha \quad \frac{\partial^2 T}{\partial r^2} + \frac{1}{r}\frac{\partial T}{\partial r} + \frac{1}{r^2}\frac{\partial^2 T}{\partial \Theta^2} + \frac{\partial^2 T}{\partial z^2} \quad \textbf{(II)}$$



a) Flat Slab



b) Cylindrical

Fig. 2. Geometric shape of breaded shrimp (T_1 = Temperature of the product's center, T_2 = Temperature of the shrimp-breading interface, T_3 = Temperature of the breading-air interface, T_∞ = Ambient Temperature, r_1 = radius of the shrimp, and r_2 = radius of the breaded shrimp).

where:

z = length of the shrimp, Ft

T = temperature, °F

r = average radius of the shrimp, Ft

Θ = degrees of rotation around the axial length of the product

The solution of equation II, as presented by Welty, Wicks, Wilson (17), is a plot of y· vs ·x, as shown in Figure 3, where:

$y = (T-T_S)/(T_O - T_S)$

$x = \alpha t/r$

T = initial uniform temperature, °F

T_s^o = surface temperature of the shrimp or temperature of the shrimp-breading interface, °F

T = center temperature of the shrimp, °F

α = thermal diffusivity, Ft^2/h

t = time, h

r = average radius of the shrimp

A flat slab being cooled or heated from one side (Fig. 4) can be used to simulate the breading layer around the shrimp. The solution for the temperature history of the breading must also satisfy Fourier's Field Equation, equation I. Assuming rectangular coordinates and finite surface and internal resistances, equation I becomes:

$$\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} \qquad \textbf{(III)}$$

For one-dimensional cooling or heating, equation III becomes:

$$\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial x^2} \qquad \textbf{(IV)}$$

The solution of equation IV, as presented by Perry's Handbook (8), is a plot of y• vs • x, as shown in Figure 5, where:

$y = (t'-t)/(t'-t)$

$x = k\Theta/\rho C_p r^2 m$

t' = temperature of the surroundings, °F

t = temperature at a given point of time, °F

t_b = initial temperature, °F

k = thermal conductivity, BTU/h · Ft · °F

Θ = time, h

ρ = density, lb/Ft^3

C_p = specific heat, BTU/lb · °F

r = distance, in the direction of heat conduction from the mid-point or mid-plane of the body to the point under consideration, Ft

$m = k/h_T r_m$

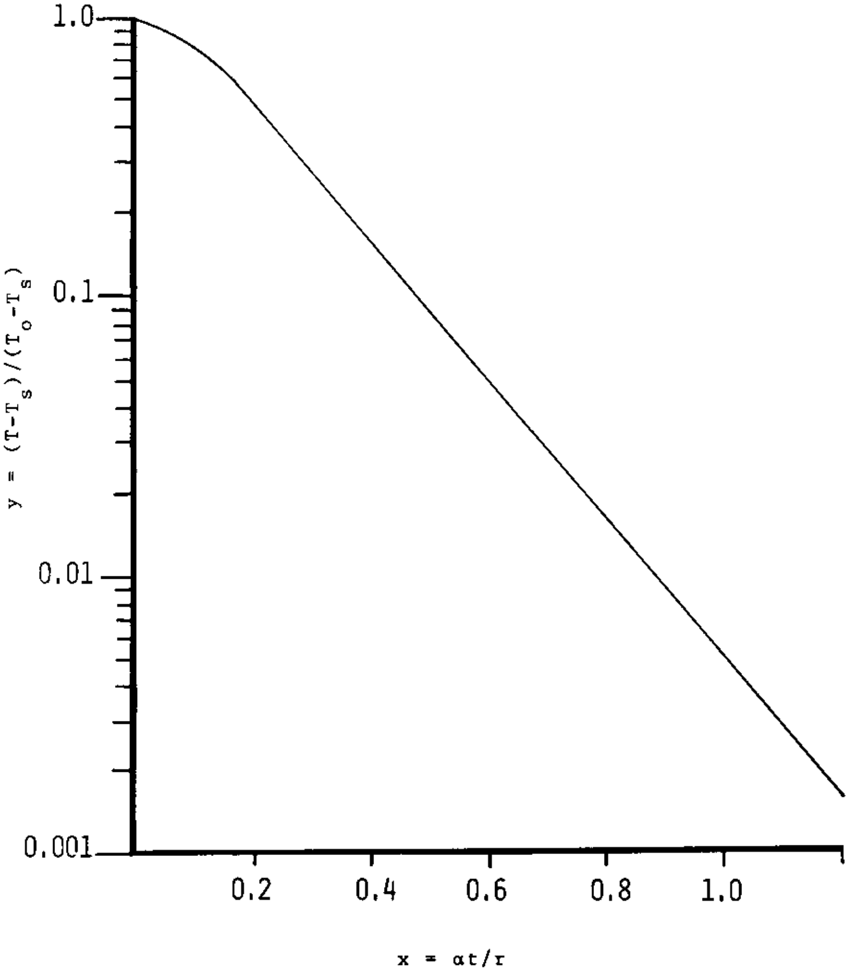


Fig. 3. The y-vs-x plot for equation II using cylindrical coordinates.

h_r = coefficient of total heat transfer between surroundings on the breading surface, BTU/h · Ft² · °F

r_m = total thickness of a slab being cooled or heated from one face, Ft

$n = r/r_m$

When the physical constants for the shrimp and breading are evaluated, equations II and IV can be solved simultaneously. Pertinent to the calculation of the temperature history is the notation that the ambient temperature, or cold storage temperature, is oscillating above and below a preset temperature. This

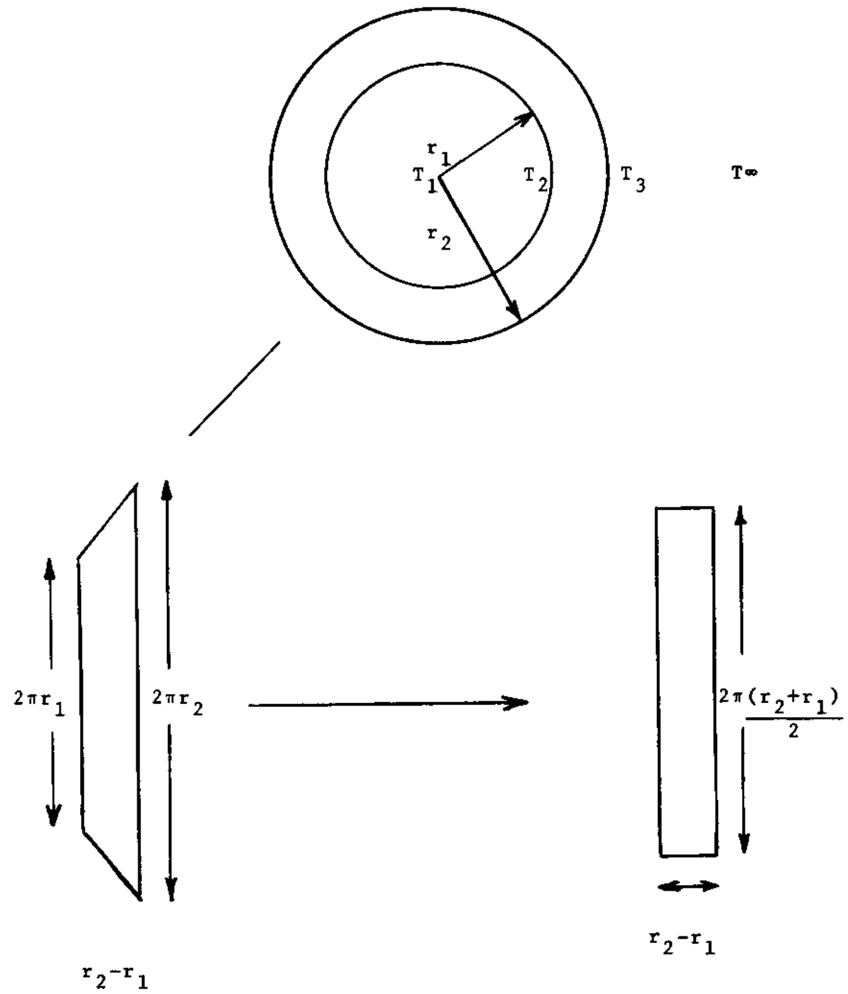


Fig. 4. Mathematical rearrangement of the breading layer shape.

oscillation of temperature is due to the nature of the temperature regulating device, ratio of cooling coil surface to the volume of the cold storage room, and the rate of air circulation in the cold storage room.

As stated previously, the temperature of the shrimp, breading, and the surroundings controls the mass transfer mechanisms occurring at a particular point in time. Evaporation, sublimation, and diffusion are the mechanisms of mass transfer involved. Evaporation and sublimation are the means by which the breading loses weight, or moisture, to the surroundings. Diffusion is the mechanism by which the shrimp loses moisture to the breading.

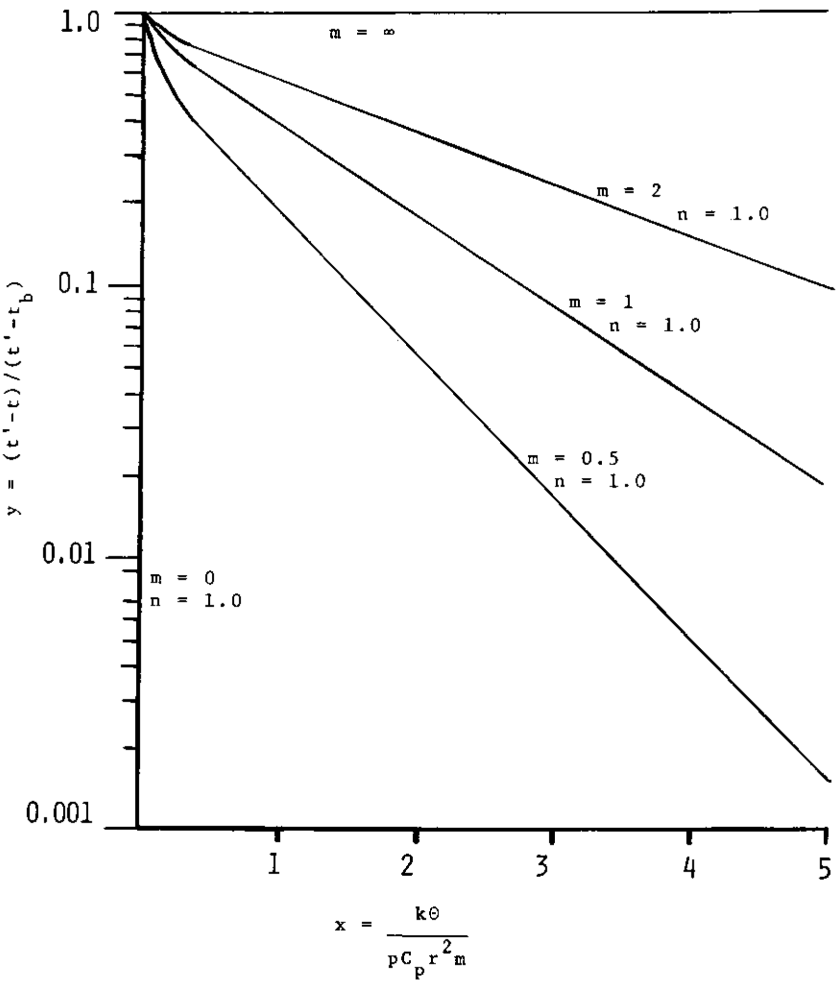


Fig. 5. Plot of y-vs-x for the solution of equation IV when heating or cooling a flat slab.

Evaporation is normally associated with the input of heat necessary to boil or vaporize a liquid. This is not so with the case under investigation. A representation of the situation encountered is shown in Fig. 6 which shows that the product is cooled by the loss of sensible heat and latent heat. Latent heat is lost by the evaporation of water from the breading-air interface. The amount of latent heat lost to the air is governed by the rate of evaporation which is dependent upon the difference in the humidities of the breading surface and the surrounding air (Fig. 1). This rate of evaporation (16) can be expressed as:

$$m = M_A k(H_i - H)A \qquad \text{(V)}$$

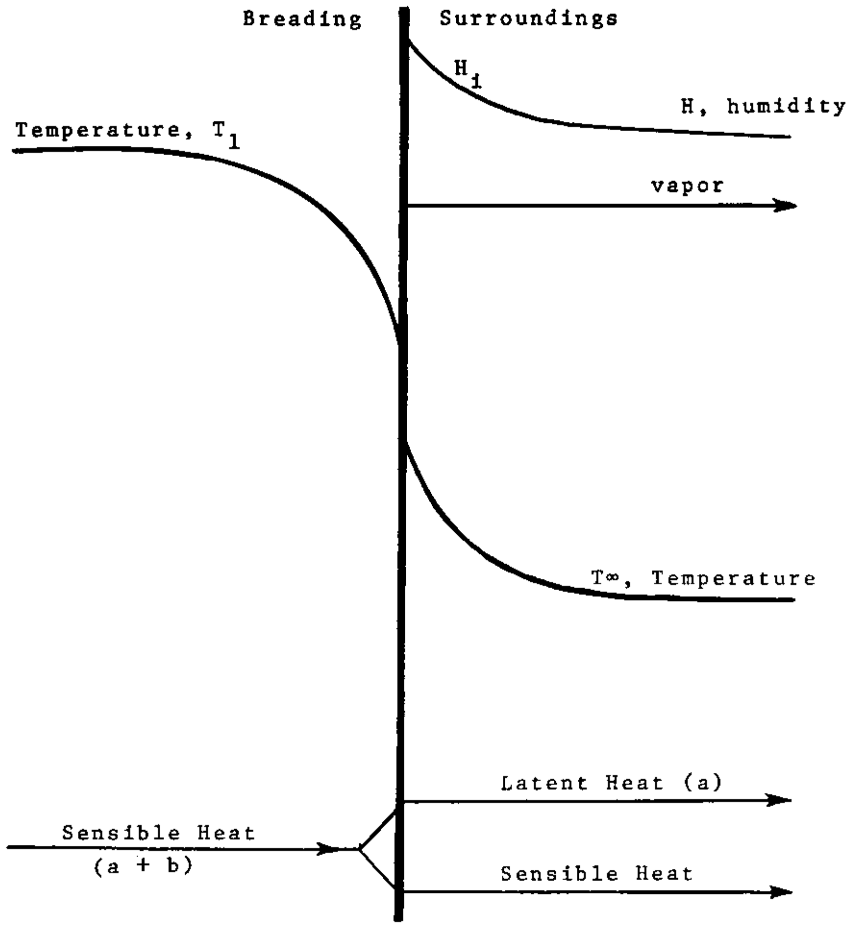


Fig. 6. Heat transfer at the breading-surroundings interface.

where:

m = rate of evaporation, lb/h

M_A = molecular weight of air, lb/lb mole

k = mass transfer coefficient, lb moles/ft^2 ·h · unit mole fraction difference

H_i = humidity of air-breading interface, lb H_2O·lb dry air

H = humidity of air, lb H_2O/lb dry air

A = evaporation area, Ft^2

Evaporation area decreases as the moisture on the breading surface freezes. When the entire breading surface is frozen, the evaporation area is zero and the moisture loss by evaporation ceases.

The temperature of the ice formed on the surface of the breading will now approach the temperature of the cold storage room. During this drop in temperature, the ice will absorb some heat from the product causing small amounts of ice to sublime. There will be periods of time when the ice temperature is lower than the ambient temperature due to the oscillation of the temperature in the cold storage room. It is this situation that allows the surroundings to act as a heat source for the sublimation of ice. The temperature difference between the ice and the surroundings is the driving force for the rate of sublimation, which can be expressed as:

$$\frac{dw}{d\Theta} = \frac{Q}{\lambda_o} = \frac{UA\Delta T}{\lambda_o} \quad \text{(VI)}$$

where:

$dw/d\Theta$ = rate of sublimation, lb/h

Q = heat absorbed by the ice, BTU/h

λ_o = heat of sublimation, BTU/lb

U = over-all heat transfer coefficient, BTU/h · ft^2 · °F

A = heat transfer area, ft^2

ΔT = temperature difference between the heat source and ice, °F

Diffusion of moisture, or moisture migration, is an added problem encountered with breaded shrimp. Shrimp contain a higher percentage of moisture than the breading material and it is this difference in percent moisture that is the driving force for diffusion. Moisture will diffuse from the shrimp to the breading giving the shrimp a negative weight change and the breading a positive weight change. While the diffusion process is occurring, the breading is losing weight by evaporation and then by sublimation. This loss of moisture by the breading increases the time necessary for the percent moisture of the breading to approach that of the shrimp. Diffusion will continue until the thermal arrest time when the moisture is immobilized by freezing.

The basic equation for the calculation of the diffusion rate can be stated as:

$$\frac{\partial x}{\partial t} = D'_v \frac{\partial^2 x}{\partial z^2} \quad \text{(VII)}$$

where:

x = average free moisture, lb H_2O/lb dry solid

t = time, h

D'_v = diffusivity, ft^2/h

z = distance measured in direction of diffusion, ft

Using cylindrical coordinates, equation VII yields upon integration:

$$\frac{x_T - x^*}{x_{T1} - x^*} = \frac{x}{x_1}$$

$$= 0.692e^{-5.78\beta} + 0.131e^{-30.5\beta} + 0.0534e^{-74.9\beta} + \ldots \qquad \textbf{(VIII)}$$

where:

$\beta = D'_v t_T / s$

D'_v = diffusivity of moisture, ft^2/h

t = time, h

s = radius of the shrimp, ft

x_T = average total moisture content at time t_T

x^* = equilibrium-moisture content

x_{T1} = initial moisture content at start

x = average free moisture content at time t_T

x_1 = initial free moisture content

(units of x are expressed in lb H_2O/lb dry solid)

Solving equation VIII for time t_T, gives:

$$t_T = \frac{s^2}{5.78\ D'_v} \ln \frac{0.692 x_1}{x}$$

If the time is plotted against the logarithim of the free-moisture content a straight line should be obtained from which D'_v can be calculated.

Data Analysis

Results of the statistical analysis of the experimental data indicated:

1. The fast freezing rate produced a much smaller weight change in the shrimp and breading as compared to the slow freezing rate.
2. For each texture of breading material used the shrimp lost approximately the same amount of weight which was, in turn, gained by the breading material. However, the fine texture lost more moisture to the surroundings than the coarse texture, resulting in a smaller change in weight of the breading material.
3. Equilibrium temperature of the breading material did not alter the moisture gained by the breading material from the shrimp. Less moisture was lost to the surroundings by the breading material at 40°F than at 82°F, resulting in a larger weight gain for the breading material at 40°F.
4. The initial weight change observed in the shrimp and breading declined as the storage time increased.

Correlation coefficients were calculated for all possible pairs of the four characteristics. Sixteen pairs were significantly correlated.

CONCLUSION

It was concluded from the results that breaded shrimp produced by using a fast freezing rate, 82°F equilibrium temperature, and fine texture breading material will produce a reduction in moisture loss by the product to the surroundings.

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