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HYDROGEN IONS PROFILES, APPARENT MOBILITY, AND DISAPPEARANCE DURING COOKING OF MEAT EMULSION—1. SLAB GEOMETRY

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ABSTRACT

A simulation model was developed by considering diffusion, convection and first order chemical reaction to predict the hydrogen ion profiles during cooking of meat emulsion slab. The model was experimentally verified for various processing conditions and the compositions of the product. There was a sharp increase of pH at the initial stage of thermal processing and it reached to a steady state value at the end of processing. The Eyring's Absolute Reaction Rate Theory described the H^+ diffusivity and reaction rate constant reasonably well. The disappearance of H^+ due to chemical reaction contributed the most in defining the H^+ profiles during processing.

INTRODUCTION

The pH of meat is important because it affects meat color, bacterial growth, and water holding capacity (WHC). Acceleration of cured meat color development is encouraged by a decrease in tissue pH. Bacterial growth is considerably reduced if pH of meat is below 5.6 (Gibbons and Rose 1950). An increase in pH raises the WHC of meat products.

Overall pH changes as a consequence of heating have been investigated by various workers (Hamm and Deatherage 1960, Paul 1964 and

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Kauffman *et al.* 1964) for various meat products. However, no work has been reported on the distribution of hydrogen ions in food products during processing.

This paper describes the movement of hydrogen ions during processing of meat emulsion slab. A simulation model was developed to predict the (H⁺) profiles and to determine reaction rate for different processing conditions and compositions of the product.

MATHEMATICAL MODELING

Assumptions

1. In a gross sense for the purposes of mathematical modeling the portion of the sausage mix which is not fat, water or salt is assumed to be protein.
2. The sausage emulsion consisted of pure meat, pure fat and additives free from fat.
3. The net movement of H⁺ is due to the solvent diffusion in liquid phase, the bulk diffusion of moisture and the depletion due to chemical reaction of first order.
4. Since the changes in the concentration of ion were small, the effective diffusivity and reaction rate constant were considered independent of concentration.
5. There is no diffusion of H⁺ upward from the top surface ($x=L$) of the horizontal slab by entrainment and no movement of H⁺ or water at the bottom of the emulsion slab ($x=0$).
6. At the beginning of the cooking process the moisture and H⁺ concentrations were uniform.

The movement of H⁺ during meat emulsion processing is a case of bulk diffusion with water, molecular diffusion and a chemical reaction. For these mechanisms the following mathematical equations were developed:

Initial conditions:

$$CI\ H\ (x,0) = CI\ H\ 0 \tag{1}$$

Boundary conditions:

$$\frac{d(CI\ H)}{dx}(L,t) = 0$$

$$\frac{d(CI\ H)}{dx}(0,t) = 0 \tag{2}$$

Mass balance:

The slab was divided into ten nodes of uniform H^+ concentration. The general mass balance equation is given by:

Rate of mass in − rate of mass out − rate of mass depletion
= rate of mass accumulation   (3)

Where

Rate of mass in or out = due to diffusion and due to convection

Diffusion of H^+ = $-DI\ H \cdot A \cdot d(CI\ H)/dx$ (4)

Convection of H^+ = $CI\ H \cdot D_m \cdot A \cdot dC/dx$ (5)

Accumulation of ions = $d(CI\ H)/dt \cdot \Delta x \cdot A$ (6)

Rate of depletion = $-KR(CI\ H - CI\ H\ E) \cdot \Delta x \cdot A$, using first order chemical reaction.   (7)

A list of symbols is given at the end.

When the mass balance equation was applied to all the ten nodes, the following ten equations were derived. These equations describe the profile of H^+ concentration with respect to time.

For node 1:

$$\frac{d(CI\ H_1)}{dt} = \left\{ -DI\ H\ \frac{(CI\ H_1 - CI\ H_2)}{\Delta x^2} \right\} - \left\{ D_{m,1} \cdot CI\ H_1\ \frac{(C_1 - C_2)}{\Delta x^2} \right\}$$
$$- \{KR(CI\ H_1 - CI\ H\ E)\}   \tag{8}$$

For node i, i=2 to 9

$$\frac{d(CI\ H_i)}{dt} = \left[DI\ H \cdot \frac{(CI\ H_{i-1} - 2CI\ H_i + CI\ H_{i+1})}{\Delta x^2} \right]$$
$$+ \left[D_{m,i-1}\ CI\ H_{i-1}\ \frac{(C_{i-1} - C_i)}{\Delta x^2} \right]   \tag{9}$$
$$- \left[D_{m,i}\ CI\ H_i\ \frac{(C_i - C_{i+1})}{\Delta x^2} \right] - [KR(CI\ H_i - CI\ H\ E)]$$

For node 10:

$$\frac{d(CI\ H_{10})}{dt} = \left[DI\ H\ \frac{(CI\ H_9 - CI\ H_{10})}{\Delta X^2} \right] + \left[D_{m,9}\ CI\ H_9\ \frac{(C_9 - C_{10})}{\Delta x^2} \right]$$
$$- KR(CI\ H_{10} - CI\ H\ E)   \tag{10}$$

To calculate the convection of H^+, the movement of moisture in the product is required during processing. This was calculated with the liquid diffusion model. Some of the terms required in this model are given below:

$$C = (m - m_e)/(m_i - m_e) \tag{11}$$
$$m_e = -0.067 \ln(-R \cdot (T + 8.495)\ln(RH) (1.096E{-}6)), \text{ for}$$
$$RH \leq 0.75 \tag{12}$$
$$m_e = -0.483 \ln(-R \cdot (T + 44.532)\ln(RH) \quad (4.584E{-}5)),$$
$$\text{for } RH > 0.75$$

These equilibrium moisture content equations are valid for $T \leq 58°C$.

$$D_m = 0.003 \exp(-0.442\ FP - 4892.7/T_a + 11.55\ C) \tag{13}$$

The details of the moisture diffusion model are given by Mittal et al. (1981). This model was used to provide the moisture concentration at various nodes in the slab processing.

Equations 8 to 10 were solved on an Amdahl 470V/6 digital computer with the Continuous System Modeling Program (CSMP).

To determine the H^+ diffusivities and the reaction rate constants of the model from the observed data, the criterion for best fit was taken as the minimum sum of normalized standard deviation δ_{HI} between predicted and the observed values of the H^+ concentration:

$$\delta_{HI} = \frac{1}{t \cdot N} \prod_0^t \sum_{n=1}^N (CI\ H_{n,exp} - CI\ H_n)^2 dt \tag{14}$$

MATERIAL AND METHODS

The experimental design chosen was a central rotatable composite design. For three variables this design consisted of 20 experiments, i.e., eight vertices of a cube (2^3 factorial), six center points for replication and six star points to give the design the property of being rotatable. Table 1 presents the variables and their levels chosen for investigations. The order of experiments was completely randomized (Mittal et al. 1979a).

Fresh emulsion was prepared before starting each experiment in the laboratory using a modified Waring Blendor. The formulation included nonfat dry milk (3%), salt (2.5%), sucrose (0.5%), corn syrup solid (2%), spices and curing agents. Protein, fat and ice were added according to the desired fat-protein ration (FP). Most of the fat was taken from the pork and protein from the lean beef.

Table 1. Variables and their levels for experiments

Variable	Variable Levels				
	−1.68	−1.0	0.0	1.0	1.68
Temperature (°C)	42	45	50	55	58
Relative humidity (%)	41	48	60	75	87
Fat-protein ratio	1.2	1.4	1.9	2.5	3.0

A closed wind tunnel was used to provide the controlled environment. The wind tunnel consisted of a fan, a heating and cooling section, steam injection system, drying column and a test section. The temperature was controlled by proportional rate and integral modes to within ±1°C. The humidity was controlled to within ±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 butterfly valve.

Meat emulsion slabs of 10.2 cm in diameter and 1.9 cm thick were employed. The emulsion was placed on an aluminum disc fitted to an aluminum ring with the help of a rubber o-ring. The side and bottom of the slab were coated with 'Castolite-AP' clear casting plastic to insure that the moisture loss was purely uni-directional from the upper surface of the slab. The details are given by Mittal *et al.* (1979a).

The hydrogen sensitive micro-electrodes were inserted in meat emulsion at different locations. Five ion-sensitive and two reference microelectrodes were inserted in one slab. The output of these microelectrodes were recorded on a 24-channel millivolt recorder. The details about instrumentation and micro-electrodes are given by Mittal *et al.* (1979b).

Calibration of Micro-Electrodes

The H^+ sensitive micro-electrodes were calibrated at 30, 50 and 70°C, and at five pH values (7, 6.5, 6, 5.4, 5). A linear relationship was found between voltage and pH at different temperatures but each microelectrode had its own calibration curve. The following model was found suitable:

$$pH = A_{11} - A_{12} \cdot EH + A_{13} \cdot T_a \qquad (15)$$

A computer program was developed to convert the recorded microelectrode output into concentration of ions with the temperatures at ion-sensitive and the reference micro-electrodes.

RESULTS AND DISCUSSION

The values of the diffusion coefficient of H^+ and the apparent first order reaction rate constant were determined with the model. The minimum normalized standard deviation between observed and predicted values of H^+ concentration was obtained with the help of a multidimensional optimization procedure. This has been developed in this study based on a pattern search algorithm of Hooke and Jeeves (1961).

Figure 1 illustrates the pH changes with time at different locations in the meat emulsion slab. It is clear that the pH is increasing at all the locations with time. In the beginning of processing there is a sharp increase of pH and at the end of processing these curves are indicating a constant pH value throughout the meat emulsion. This constant value was considered to be the equilibrium value of H^+ concentration.

The following model was found suitable for these equilibrium H^+ concentration values, which was obtained after applying the Nonlinear Regression Analysis of the Statistical Analysis System, SAS (Barr *et al.* 1976), giving unadjusted r^2 value of 0.999:

$$pH_{eq} = 0.011 \ T_a \cdot \exp((0.0082 + 0.0021 \ RH) \cdot FP + 153.8/T_a) \quad (16)$$
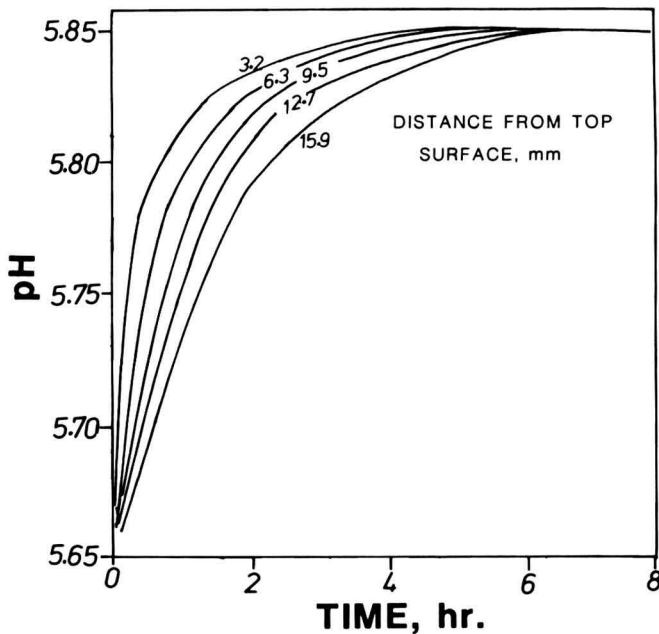
FIG. 1. THE pH CHANGES AT DIFFERENT DEPTHS IN THE MEAT EMULSION

The increase of pH units of 0.16 to 0.30 was noticed in these experiments. The minimum increase was at 42°C and maximum at the processing temperatures of 55 and 58°C.

Empirically it has been found that heating usually increases the pH. For example, Kauffman *et al.* (1964) found that the pH of pork muscle usually increased about 0.35 units on cooking. Hamm and Deatherage (1960) found an increase of about 0.4 pH units in beef, while Paul (1964) found an increase of about 0.3 units in rabbit muscle. All of these studies were undertaken at cooking temperatures of 68 to 74°C. Wierbicki *et al.* (1957) also noted the increase in pH of muscle during heating. Bendall and Wismer-Pedersen (1962) found a pH increase of about 0.3 pH unit in the intact muscle with all its natural buffers present during heating between 65 and 70°C.

The pH changes that occur during heating may be caused by charge changes or hydrogen bonding, or both, within the myofibrillar proteins (Hamm 1966). This has been explained by splitting of hydrogen bonds which should release additional positive charges. The heating may cause the formation of new hydrogen bonds around the isoelectric point of actomyosin. During heat-coagulation of tissue myofibrils, actomyosin and the number of dye-binding acidic groups of protein decrease.

Hamm and Deatherage (1960) reported that between 30 and 40°C a mild denaturaton occurs, resulting in an unfolding of protein chains and in the formation of new salt and/or hydration bonds. A stronger denaturation starts at 40°C and continues to 50°C. The changes in this range of temperature are mainly determined by the disappearance of acidic groups in the muscle proteins.

A decrease in acidic groups also takes place between 50 and 55°C. Hydration is decreased between 55 and 80°C but not so markedly as between 40 and 50°C. In this range of temperature the new cross-linkages may be forming and the loss of acidic group is observed (Hamm and Deatherage 1960).

Sugar is reported to decrease pH considerably at levels above 0.5% (Ockerman 1974). The sodium citrate and citric acid decrease the pH while NaCl is said to increase it. No effect on pH due to the addition of salts of NO_2, NO_3 and sodium erythorbate was noted.

The above mentioned presentation indicates that the mechanisms of pH change during meat heating are complex.

In this study, since H^+ concentrations are small and changes apparently are smaller, a first order reaction was assumed and it was further assumed that only 'active' concentration of hydrogen ions in excess of the apparent equilibrium (CI H $- CI$ H E) is taking part in the chemical reaction.

Figure 2 illustrates the predicted and experimental values of the H^+ concentrations at various locations in the slab. This shows the typical results out of 20 experiments. There is a good agreement between the experimental and predicted values in the beginning and at the end of cooking. In between there is some deviation; however, this can be ignored on the ground that the total deviations are small. The normalized standard deviation values are between 0.100E−6 and 0.325E−6.

Models for *DIH* and *KR*

The values of the diffusivity of H^+ (*DI* H) and first order reaction rate constant (*KR*) were calculated for various processing conditions and the compositions of the product. These parameters were considered to be independent of ion concentration, since the changes in the concentration of H^+ during whole cooking period is small. However, it was found that these parameters depend upon product temperature and FP.

The Eyring's Absolute Reaction Rate Theory (Aiba *et al.* 1973) was employed to fit suitable models for these parameters. This approach has
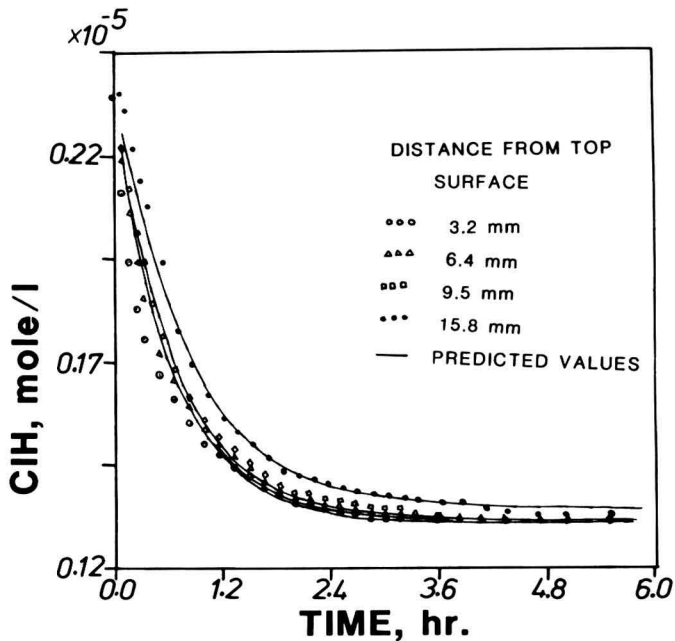
FIG. 2. COMPARISON OF THE PREDICTED AND OBSERVED VALUES OF H⁺ CONCENTRATION AT DIFFERENT DEPTHS IN THE MEAT EMULSION SLAB OF 1.9 FP DURING COOKING AT 50°C AND 60% RH

already been discussed by Mittal *et al.* (1979a). Based of this theory the following models were fitted. The unadjusted r^2 values of 0.98 and 0.95 were obtained for the models of *DI* H and *KR*, respectively.

$$DI\ H = c_1 T_a \cdot \exp(c_2 FP + c_3/T_a)$$
$$KR = c_1 T_a \cdot \exp(c_2 FP + c_3/T_a)$$

(17)

The estimate of the coefficients and their asymptotic standard error of estimate are given in Table 2. In general, the values of the standard error of the estimate are large; however, the models were able to predict the values of *DI* H and *KR* reasonably well ($r^2 > 0.95$).

The diffusivity of H^+ is increasing exponentially with the increase in temperature and fat-protein ratio, while the apparent reaction rate constant is increasing exponentially with the increase in temperature and the decrease in FP.

Preliminary sensitivity analysis indicated that the changes in the diffusion coefficients of H^+ and water up to 12% do not affect the predicted values appreciably. However, the changes in the reaction rate constant $> 8\%$ is more critical. The results also indicate that the disappearance of H^+ is the single most significant factor affecting the concentration of H^+. The contribution of diffusion due to concentration gradient and the convection due to the mobility of water is 10 to 20% in the H^+ concentration changes.

Table 2. Estimate of the coefficients of *DI* H and *KR* models

Coefficients	Estimate		Asymptotic Standard Error of Estimate	
	DI H	*KR*	*DI* H	*KR*
c_1	2.784E−8	1.731E−3	7.750E−8	7.628E−3
c_2	0.095	−0.230	0.077	0.132
c_3	217.0	397.4	897.0	1421.0

Thermodynamic Properties

From the models of diffusivity and reaction rate constant, the values of activation energy and entropy for the H^+ diffusion and reaction were calculated. These are given by:

$$\Delta H^* = -c_3 \cdot R$$

$$\Delta S^* = c_2 \cdot FP \cdot R$$

(18)

The activation energy for the net diffusion of H^+ is -430 cal/mole and for the chemical reaction is -790 cal/mole. The values of the entropy of activation for the diffusion of H^+ vary between 0.22 and 0.57 cal/(mole·K) and for the chemical reaction vary from -0.54 to -1.37 cal/(mole·K) depending on the FP. The initial moisture content in the product was decreasing with the increase in FP. Due to the large standard error of the estimates of c_2 and c_3, the values of ΔH^* and ΔS^* will vary greatly.

For bimoleculear reactions, the entropy of activation is generally negative because of the 3-degrees of translational freedom which are lost when the two reacting molecules collide to form a single activated complex (Hisrchfelder et $al.$ 1954). Eagland (1974) found that the transfer processes are dominated by negative ΔS^0, presumably due to the pronounced water 'structuring' caused by the hydrophobic hydration that arises on transfer of the side chains from the hydrocarbon medium to the water. The ΔS^0 for helix formation in heat denaturation of protein was reported to be -2.9 cal/(mole·K) by Eagland (1974). The absolute values of ΔS^* obtained in the present study is lower than ΔS^0.

In order to interpret the apparent chemical reaction or disappearance of H^+, we can first turn to the kinetics of protein denaturation since pH increase is occurring simultaneously with the coagulation of proteins.

The rate constants for a reversible two-state process depend only on the maximum activation free energy that has to be traversed on the pathway from native to denatured. Tanford (1970) found the overall change in ΔH^0 from -120 to 105 kcal/mole for ribonuclease and -180 to 115 kcal/mole for β-lactoglobulin by choosing the reaction native$\rightleftharpoons$random coil for protein denaturation by heat. The values of ΔH^* (activation) obtained in the present investigations are in the order of 1/200th of the above values, and it is likely that protein changes are not the principal cause but may be influenced by mechanisms that caused the pH change.

The activation free energies, ΔG^*, for the diffusion of H^+ are between -615 and -500 cal/mole and for chemical reaction the values varied between -615 and -350 cal/mole. By combining different alternative possibilities Tanford (1970) arrived at ΔG^0 values for the native$\rightleftharpoons$random coil transition that range from -88 to -395 kcal/mole for ribonuclease and -70 to -525 kcal/mole for β-lactogloblin. Piez and Sherman (1970) also obtained similar values for the reversion of the peptide to a collagen type triple helix. The ΔH^0 for helix formation was reported to be -9600 cal/mole by Eagland (1974). The values from our study, which are, of course, for activated state, are much lower than these values.

Reaction Kinetics

To study the kinetics of H^+ disappearance further, the following reactions were also considered:

$$\frac{d}{dt}(CI\ H) = -KR(CI\ H - CI\ H\ E)^n \tag{19}$$

$$\frac{d}{dt}(CI\ H) = -KR(CI\ H - CI\ H\ E)^n (m - m_e)^p \tag{20}$$

$$\frac{d}{dt}(CI\ H) = \frac{-V_m \cdot (CI\ H - CI\ H\ E)}{K_m + (CI\ H - CI\ H\ E)} \tag{21}$$

The concentration of H^+ were predicted with these equations in the simulation model for the six central points of the experimental design for comparison. On the basis of the minimum δ_{HI}, it was found that the Michaelis-Menten equation (21) is more appropriate. The values of δ_{HI} were less by 24 to 71% than the values obtained from the model using first order reaction rate.

The values of 'n' in Eq. (19) were between 0.9 and 1.0, and in Eq. (20) were between 1.0 and 1.1. This implies that the assumption of first order reaction seems to be appropriate. However, the Michaelis-Menten equation describes the H^+ disappearance more closely.

CONCLUSIONS

1. The mathematical model developed by considering diffusion, convection and first order chemical reaction was able to predict hydrogen ions concentration reasonably well.
2. The pH increased at all the locations in the slab with time. There was a sharp increase of pH at the beginning of thermal processing and the pH reached to steady state value at the end of processing. The increase of 0.16 to 0.30 pH units was observed between 42 to 58°C.
3. The values of $DI\ H$ vary from 0.170E−4 to 0.278E−4 m^2/h and of KR from 0.79 to 1.78 1/h.
4. The Eyring's Absolute Reaction Rate Theory describes the H^+ diffusivity and reaction rate constant reasonably well. These parameters were found to be the functions of temperature and the composition of the product.
5. The values of the entropy of activation for the diffusion of H^+ vary between 0.22 to 0.57 cal/(mole·K) and for the chemical reaction vary from −1.37 to −0.54 cal/(mole·K).

6. The free energies of activation for the diffusion of H^+ are between -615 to -500 cal/mole and for chemical reaction between -615 and -350 cal/mole.

NOMENCLATURE

A cross section area of slab, m^2
C concentration of water, dimensionless
$CI\,H$ H^+ concentration, mole/liter
$CI\,H\,E$ equilibrium concentration of H^+, mole/liter
$CI\,H\,O$ initial concentration of H^+, mole/liter
D_m diffusivity of water, m^2/h
$DI\,H$ diffusivity of H^+, m^2/h
$E\,H$ output of H^+ sensitive micro-electrode, mV
FP fat protein ratio
KR reaction rate constant, $1/h$
K_m reaction rate constant in Michaelis-Menten equation
L slab thickness, m
N number of experimental nodes in ions concentration profile
R gas constant
RH relative humidity, decimal
T temperature, °C
T_a absolute temperature, K
V_m constant in Eq. (21)
m moisture content, decimal dry basis
n constant in Eq. (19) and (20)
p constant in Eq. (20)
r^2 coefficient of determination
t time, h
x distance, m
ΔG free energy, cal/mole
ΔH enthalpy, cal/mole
ΔS entropy, cal/(mole·K)
Δx slice thickness, m
$\delta_{H I}$ normalized standard deviation

Sub-script
  e equilibrium
  i initial

n node number

exp experimental

$1\text{-}10$ node number

super-script

0 equilibrium state

*   activation state

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HYDROGEN IONS PROFILES, APPARENT MOBILITY AND DISAPPEARANCE DURING COOKING OF MEAT EMULSION—2. CYLINDRICAL GEOMETRY

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ABSTRACT

The modeling techniques developed in the first part of this series were applied to describe the hydrogen ion profiles in meat emulsion in cylindrical shape during thermal processing at temperatures $>58°C$. The model was verified with experimental data collected at various processing conditions and the compositions of the product. An increase of 0.27 to 0.50 pH units was recorded in the processed product. The values of reaction rate constant varied between 0.88 to 2.90 1/h and the diffusivity of H^+ was constant at $0.2E-5$ m^2/h.

INTRODUCTION

In this investigation, the diffusion dynamics of hydrogen ions during thermal processing of meat emulsion in a frankfurter geometry was studied for various processing conditions and compositions of the product. Simulation model was developed to describe the movement and distribution of these ions in the product during cooking. The first order reaction rate constant for the H^+ disappearance was also determined. These studies at higher temperatures than the studies in a temperature uniform slab geometry provide a test of the earlier hypothesis for a realistic product and process.

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MODELING

An approach was developed for modeling H^+ movement in the meat emulsion slab during cooking in the first part of this series. A similar approach has been used here for a cylindrical geometry. Assumptions developed in the last paper are also applicable here. The initial and boundary conditions are given below:

Initial conditions:

$$CI\ H\ (r,0) = CI\ H\ O \tag{1}$$

Boundary conditions:

$$\frac{d}{dr} CI\ H\ (0,t) = 0 \tag{2}$$

$$\frac{d}{dr} CI\ H\ (R,t) = 0 \tag{3}$$

Mathematically, different mechanisms of ions transport can again be written as:

$$\text{Diffusion of ions} = -DI\ H \cdot A \cdot dCI\ H/dr \tag{4}$$
$$\text{Convection of ions} = CI\ H \cdot D_m \cdot A \cdot dC/dr \tag{5}$$
$$\text{Accumulation of ions} = dCI\ H/dt \cdot V \tag{6}$$
$$\text{Rate of depletion} = -KR(CI\ H - CI\ H\ E) \cdot V \tag{7}$$

The cylinder was divided into ten radial sections. Again, the concentration of ions was assigned to the center of each node. Based on the conservation of mass principle, the following equations were developed for the change in concentration of ions at various nodes:

For node 1:

$$\frac{d}{dt} CI\ H_1 = \left\{ 2 \cdot \frac{DI\ H}{r_1} \cdot \frac{(CI\ H_1 - CI\ H_2)}{\Delta r} \right\}$$
$$- \left\{ 2CI\ H_1 \cdot \frac{D_{m,1}}{r_1} \cdot \frac{(C_1 - C_2)}{\Delta r} \right\} - KR(CI\ H_1 - CI\ H\ E) \tag{8}$$

For node i, $i = 2$ to 9

$$\frac{d}{dt} CI\ H_i = \frac{2}{\Delta r(r_1^2 - r_{i-1}^2)} \Big[DI\ H \{r_{i-1}(CI\ H_{i-1} - CI\ H_i)$$
$$- r_i(CI\ H_i - CI\ H_{i+1})\} + CI\ H_{i-1} D_{m,i-1} \cdot r_{i-1}(C_{i-1} - C_i)$$
$$- CI\ H_i \cdot D_{m,i} \cdot r_i(C_i - C_{i+1}) \Big] - KR \cdot (CI\ H_i - CIHE) \tag{9}$$

For node 10:

$$\frac{d}{dt} CI\,H_{10} = \frac{2 \cdot r_9}{\Delta r(R^2 - r_9^2)} \{DI\,H\,(CI\,H_9 - CI\,H_{10})$$

$$+ CI\,H_9 \cdot D_{m,9}(C_9 - C_{10})\} - KR(CI\,H_{10} - CI\,H\,E) \tag{10}$$

Simultaneous heat and mass transfer model with a Fickian type liquid diffusion predicted the temperature and moisture profiles during processing. The details of the model are given elsewhere (Mittal and Blaisdell 1982). Some of the terms are given below:

$$C = (m - m_e)/(m_i - m_e) \tag{11}$$

$$m_e = -0.102 \ln(-R_g \cdot FP \cdot (T + 5.665) \cdot \ln(RH) \cdot (1.132E\,-7)) \tag{12}$$

This equation is valid for the experimental conditions used in the investigations.

$$D_m = \exp(8.679 + 0.135\,FP - 4341.5/T_a + 8.55\,C) \tag{13}$$

The thermo-physical properties of the frankfurter used in the simulation are tabulated in Table 1.

Equations 8 to 10 were solved on an Amdahl 470 V/6 digital computer using the IBM Continuous System Modeling Program (CSMP). To determine the values of the diffusivity of H^+ and reaction rate constant from the observed data, the criterion for best fit was taken as the minimum sum of normalized standard deviation δ_{HI} between computed and observed values for ions concentration profile. This was defined in the first part of this series.

Table 1. Thermophysical properties of frankfurter

Thermal conductivity	1.55 kJ/(h·m·K)	(Agrawal 1976)
Specific heat	3.39 kJ/(kg·K)	(Riedel 1956)
Latent heat of vaporization	2326 kJ/kg	
Heat transfer coefficient	Function of Temperature	(Kern 1950)
Density	965 kg/m^3	
Thermal diffusivity	4.76×10^{-4} m^2/h	

MATERIAL AND METHODS

The experimental design was a central rotatable composite design. Table 2 presents the variables and their levels chosen for investigations. Other experimental details are described in the first part of this series.

Table 2. 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

Meat emulsion was stuffed into polyethylene casing of 2.54 cm in diameter with the help of a hand operated stuffer. Various identical frankfurters of about 15.2 cm length were used in this study. 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.

Four H^+-sensitive and one reference micro-electrodes were inserted in the frankfurter from one end. A multi-holed plastic spacer was used to keep the mirco-electrodes in axial and at the prescribed radial positions. High vacuum grease was applied to avoid any leakage of fluid.

The values of the diffusion coefficient of H^+ and the apparent first order reaction rate constant were determined using the model. The minimum normalized standard deviation was obtained with a multi-dimensional optimization program as explained in the last paper.

RESULTS AND DISCUSSION

Figure 1 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 processing there is a sharp decrease of concentration and at the end of processing these curves are indicating an apparent equilibrium pH value.

The following model for these equilibrium H^+ concentration values was obtained after applying the Non-linear Regression Analysis of the Statistical Analysis System, (SAS) (Barr et al. 1976), giving an unadjusted coefficient of determination of 0.99:

$$pH_{eq} = 0.0113 \ T_a \exp((4.131E-3 + 2.329E-3 \, RH)FP + 148.9/T_a)$$

$$(14)$$
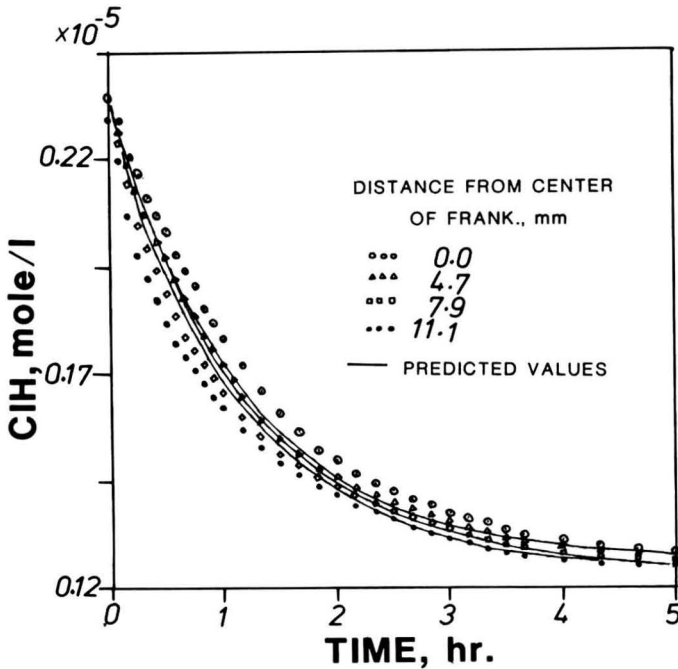
FIG. 1. DISTRIBUTION OF H^{+} CONCENTRATION DURING COOKING OF FRANKFURTER AT 58°C, 60% *RH* AND 1.9 *FP*

An increase of 0.27 to 0.50 pH units was noted in these experiments. The minumum increase was at 58°C and maximum was at a temperature of 76°C. The increases in pH units in frankfurters were approximately 67% more than the increases in pH observed for slab processing. It is believed to be due to the low processing temperatures used in the slab processing.

The mechanisms of H^{+} concentration changes are not known in detail. However, according to Hamm (1960) the pH and the amount of carboxyl groups are changed by an increase in temperature in the 55 to 80°C range, but not so markedly as between 40 and 50°C. The formation of free H_2S starts at temperatures above 80°C and increases with increase in temperature. Hamm (1966) pointed out that heating of myofibrils at 70°C does not influence the content of glutamic acid, aspartic acid, tyrosine and crysteine. The increase in available dye-binding imidazolium groups (around pH 5) lowers the number of available dye-binding acidic groups (around pH 6) because of the formation of salt-like cross linkages between acidic and imidazolium groups.

Figure 1 illustrates the predicted and experimental values of the H^+ concentrations at various locations in the frankfurter. This is a typical result out of 20 experiments. There is a good agreement between the experimental and computed values in the beginning and at the end of cooking. Between these stages deviations in the order of 0.015 pH unit or less are visible in Figure 1. The H^+ concentration for nodes near the surface respond faster and interior nodes slightly slower than predicted values in the initial period. This might be due to the under-estimation of surface H^+ levels and/or due to the difference in temperature between reference and H^+-sensitive micro-electrodes. The normalized standard deviation varied from 0.0680E−6 to 0.2218E−6. For six central points of the design, the average δ_{HI} was 0.1066E−6 with a standard deviation of 0.0161E−6.

Figure 2 shows the deviation between experimental and predicted values of H^+ concentration with time at the center and 7.9 mm from the center of the frankfurter. The temperatures at these nodes are also

FIG. 2. DEVIATION BETWEEN EXPERIMENTAL AND PREDICTED VALUES OF H^+ CONCEN-
TRATION (SOLID LINES) AND TEMPERATURE (DOTTED LINES) AT TWO LOCATIONS
IN FRANKFURTER DURING COOKING AT 69°C, 60% RH AND 1.9 FP
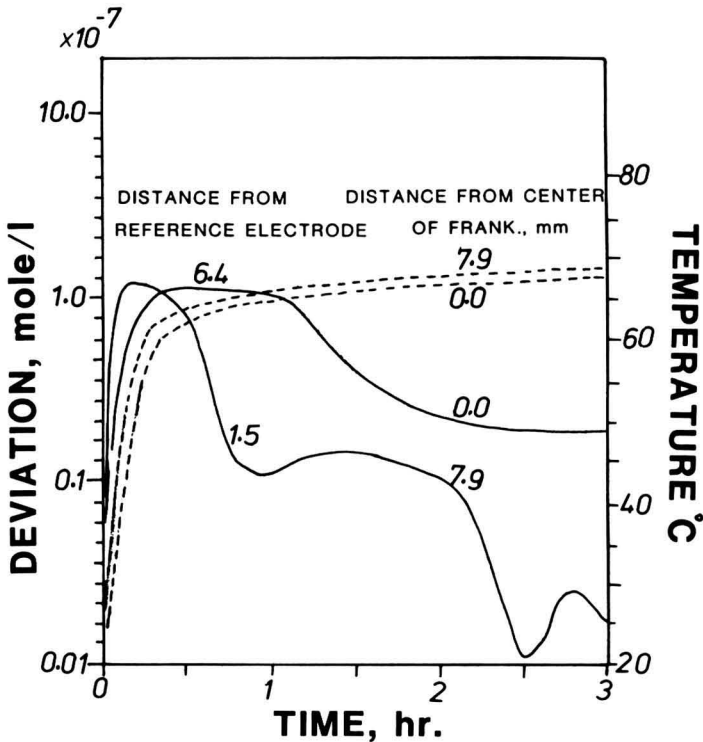
shown. The central node was 6.4 mm inward from the reference micro-electrode and the other was at a distance of 1.5 mm. This figure illustrates the size of error introduced by using one reference micro-electrode due to the existence of temperature gradient. The deviations are greater in the initial period of cooking perhaps due to the greater temperature gradient and the come up time of the electrodes. These deviations are decreasing with time as the temperature gradient is diminishing. The deviations are more at the central node perhaps due to the greater distance of reference micro-electrode from this node. Thus some error was introduced due to the use of one reference micro-electrode. However, it was not possible to install more than one due to the small diameter of frankfurter. Larger diameter of frankfurter would have changed the assumption of one dimensional flow.

Diffusivity and Reaction Rate Constant

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 1/h. The minimum value is at the minimum processing temperature (58°C) and the maximum value is at 69 and 76°C. Thus the reaction rate constant is increasing with the increase in temperature. In slab processing (part one of this series) the values of KR varied from 0.79 to 1.78 1/h. The higher values of the KR in frankfurter processing are believed to be primarily due to the higher temperatures, but the transport mechanisms may also shift as other proteins or salt become involved. For six central point of the design the average of KR was 2.53 1/h with a standard deviation of 0.43 1/h.

The values of the diffusivity of H^+ were found to be constant (not significantly influenced by the experimental conditions) at 0.2E-5 m^2/h for various test conditions. In the slab processing experiments, the values of diffusivity varied from 0.170E^{-4} to 0.278E-4 m^2 h, and were the functions of temperature and FP.

The exact reason for the constant diffusivity of H^+ in frankfurter cooking at higher temperatures is unknown at this time. A possible reason might be the maintenance of electrical neutrality of the solution in the frankfurter. The other ions present in the solution, as well as the particular counter ions which accompany the ion, will also influence the net effective diffusion rate. Also in the cylindrical geometry at higher temperature processing, the temperature changes at different nodes were more significant than during slab processing at low temperatures. The assumption of constant thermal properties in the model will also influence the moisture diffusivity calculations.

The reference electrode temperature uncertainties, temperature changes with time, some uncertainties in thermal properties and the

computation problems of multi-variable optimization in large systems are primarily responsible for the differences between simulated and observed H^+ concentrations at intermediate times.

Some error might have been introduced by the use of first order reaction for H^+ disappearance, since exact kinetics was not known. In the first part of this series, it was found that the Michaelis-Menten equation is predicting H^+ disappearance closer to experimental values. This was not used for frankfurter due to the large simulation time requirement.

From previous experience (part I) it was presumed that the KR for H^+ depletion is the function of temperature and FP. The Eyring's Absolute Reaction Rate Theory was employed to fit a suitable model for KR . Based on this theory, the following model was fitted, giving an unadjusted coefficient of determination of 0.96:

$$KR = c_1 T_a \cdot \exp(c_2 FP + c_3/T_a) \qquad (15)$$

where, $c_1 = 785.11 \pm 2337.8$ (asymptotic standard error of estimate)
$\quad c_2 = -0.133 \pm 0.114$
$\quad c_3 = -3935 \pm 1024$

The corresponding values of c_1, c_2 and c_3 for slab processing at low temperatures were 0.0017, −0.230 and 397, respectively. The values of c_1 and c_3 are quite different in both models. In the frankfurter processing, the DI H is constant, and the moisture concentrations were simulated by applying a simultaneous heat and mass transfer model (Mittal and Blaisdell 1982). In cylindrical geometry the temperature changes were a more significant portion of the process than in the slab configuration. The experimental variability was reflected in the KR model, and some of the temperature effects were shared by other kinetic parameters such as moisture diffusivity.

There is a large difference and change in sign in the value of c_3, which is a measure of ΔH^*, for slab and frankfurter geometries. The reason is not clear. For heat denaturation of proteins, which is taking place simultaneously with pH changes, the negative and positive values of ΔH^* were reported (Tanford 1970 and Eagland 1974). However, these reported values for protein denaturation by heat are 50 to 100 times more than the values calculated for H^+ mobility and disappearance. According to Tanford (1970), the changes in sign and wide variation in the heat denaturation of protein is due to the fact that the precisely folded polypeptide chain unravels piece by piece and passes through states with increased disorder and increased exposure to hydrophobic and peptide groups to the solvent. It may also be true for H^+ kinetics.

Further if one is at the saddle point for the shift between two mechanisms as Aiba *et al.* (1973) have shown for microbial growth, small value and shift in sign will follow. The energy value or more likely the level of salt structural water intractions or the mobility of H^+ to an unfolding ionizing residual may be other reasons.

Kinetics of H^+ Disappearance

To further investigate the kinetics of H^+ disappearance during the cooking of frankfurter Fig. 3 and 4 were drawn. Figure 3 shows the relationship between $\log(CI\ H - CI\ H\ E)$ and time for the two nodes.

For first order reaction, the slope of these lines should be equal to $KR/2.303$. Based on this the values of KR are 1.61 and 1.84 1/h for the central and 7.9 mm from the center of the frankfurter nodes. The actual KR was computed to be 2.09 1/h, which is 30 and 14% higher,
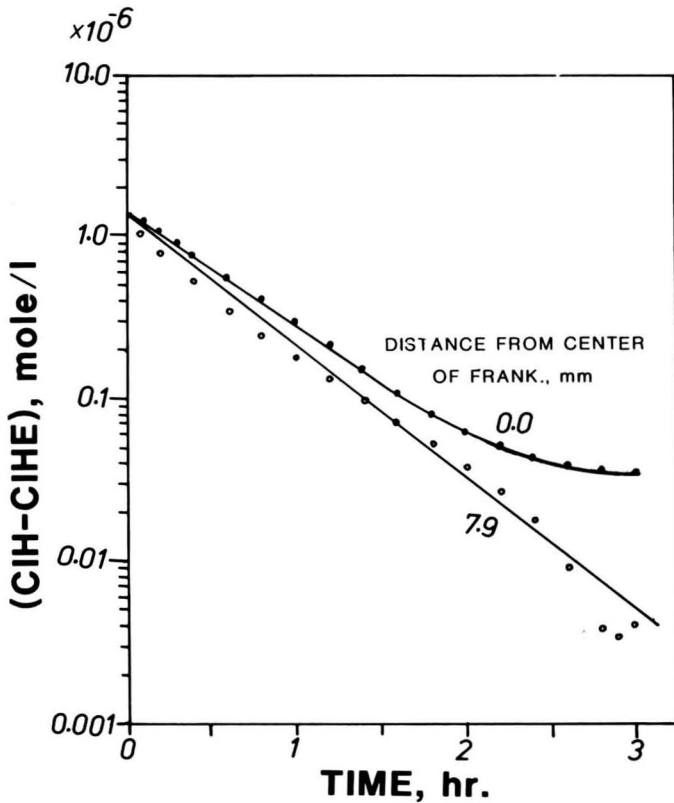
FIG. 3. LOG (*CI H – CI H E*) VERSUS TIME FOR THE COOKING OF FRANKFURTER AT 69°C, 60% *RH* AND 1.9 *FP*
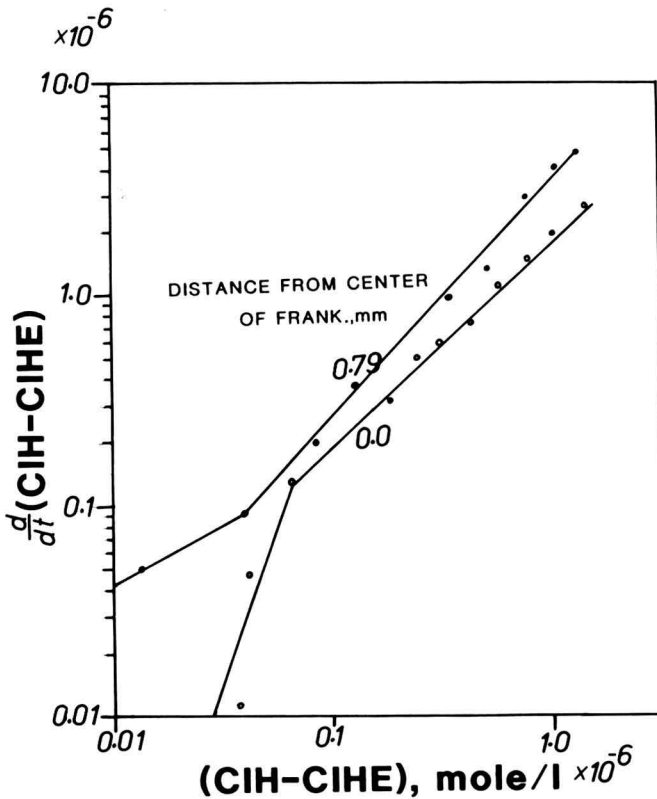
FIG. 4. RATE OF CHANGE OF H$^+$ CONCENTRATION WITH TIME VERSUS (CI H – CI H E) ON
LOG-LOG SCALE FOR THE COOKING OF FRANKFURTER AT 69°C, 60% RH AND 1.9 FP

respectively than above values. The concentration of H$^+$ is also chang-
ing due to the diffusion and convection of H$^+$ in addition to chemical
reaction, hence the assumption of the first order reaction seems to be
valid up to 75% of the time.

Figure 4 illustrates the rate of change of concentration of H$^+$ with
time versus (CI H $-CI$ H E) on log-log scale for similar nodes. These
can be represented by two straight lines. The slopes of these lines are
−1.0 and −1.11 for the central and 7.9 mm from the center of
frankfurter nodes respectively, for the initial 67% processing time. At
the later stages of cooking the slope at the central node is −3.0 and at
the other node is −0.57. This shows that a first order reaction for the
disappearance of H$^+$ is working for the 67% of the processing time. At
the later stages of cooking varying order of reaction may be working
at diffeent locations of the frankfurter.

NOMENCLATURE

A cross sectional area of frankfurter, m^2
C concentration of water, dimensionless
$CI\,H$ H^+ concentration, mole/liter
$CI\,H\,E$ equilibrium concentration of H^+, mole/liter
$CI\,H\,O$ initial concentration of H^+, mole/liter
D_m diffusivity of water, m^2/h
$DI\,H$ diffusivity of H^+, m^2/h
FP fat-protein ratio
KR reaction rate constant, $1/h$
R radius of frankfurter, m
R_g gas constant
RH relative humidity, decimal
T temperature, °C
T_a absolute temperature, K
V volume of frankfurter section, m^3
m moisture content dry basis, decimal
pH_{eq} equilibrium value of pH
r distance in radial direction, m
t time, h
Δr small increment in radial direction, m
ΔH^* activation energy, cal/mole
δ_{HI} normalized standard deviation

Subscript

e equilibrium
i initial
$1\text{-}10$ node number

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THE EFFECT OF APPLE MATURITY AND FIRMNESS ON BRUISE VOLUME[1]

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ABSTRACT

Red and Golden Delicious apples were tested to determine resistance to impact bruising with respect to day after bloom. Impact resistance measured by volume of bruised tissue was found to have a significant linear relation to day after bloom, firmness and bruise energy. Specific bruise volume (bruise volume per unit of energy input) did not change significantly over the growth period of the fruit when a constant drop height was maintained. This indicates that increases in bruising as the apple matures are due to increased weight of the fruit (bruise energy) rather than change in properties of the apple tissue.

INTRODUCTION

Impact bruising of apples during mechanical harvesting limits the use of the harvester primarily to processing fruit. Furthermore, Diener *et al.* (1981) have shown that stage of maturity can apparently cause large variations in the amount of bruising resulting from mechanical harvesting, but a corresponding change in bruising did not appear to occur in hand harvested samples from the same orchards . This leads to the concensus as stated by Hyde and Ingle (1968) and other researchers that apples are more easily bruised as they approach maturity. Since the bruise susceptibility of apples from impact is apparently magnified when mechanically harvesting apples, it is important to determine how this property changes with maturity.

The mechanics of impact has been studied at length by several authors using several different techniques and arriving at different conclusions.

It was demonstrated by Clevenger and Hamman (1968), Mohsenin (1970), Mohsenin and Goehlich (1962), Morrow and Mohsenin (1966), Wright and Splinter (1968) and Diener and Dubbe (1970) that biological materials such as apples have viscoelastic behavior and as such are sensitive to loading rate.

Impact energy to produce a given bruise was found to be greater than that required for the same bruise volume applied under slow loading. This was demonstrated by Fridley and Adrian (1966), Wright and Splinter (1968), Fletcher et al. (1965) and Hammerle and Mohsenin (1966).

Impact Apparatus

Most impact test equipment have used one of the following princi-ples: (1) a fruit free fall, (2) a pendulum drop or (3) a falling mass which impacts the fruit. The free fall method has the advantage that the apparatus is simple and this technique duplicates the way apples impact the catching frame (Mohsenin et al. 1978 and Diener et al. 1979). It has a disadvantage in that fruit may rotate during drop and the location of impact on the fruit cannot be precisely predicted.

A pendulum device as used by Fridley et al. (1964), Bittner et al. (1968) holds the fruit against a stationary support and impacts it with a pendulum arm. An energy balance was developed for the pendulum test in which total impact energy was equated to energy absorbed by the support, fruit bruise energy and fruit rebound energy.

The falling mass technique has the advantage of simple construction and can be instrumented easily (Wright and Splinter 1968 and Fluck and Ahmed 1973). Chen and Sun (1981) used a falling rod with a 1.25 cm diameter spherical tip. The rod was mounted on a graduated vertical post and propelled into the fruit using an electromagnet. In this study they found that bruise volume correlates linearly with impact energy for Golden Delicious apples. However, they found no clear relation between bruise volume and impact velocity.

Failure Theory

The mechanics of failure has been postulated by several authors using different criteria. Horsfield et al. (1972) used the Hertz theory for impact of two spheres. This theory assumes that failure is due to excessive internal shear rather than the amount of energy absorbed. This theory shows that shear stress is proportional to: (1) impact energy, (2) elastic modulus of the fruit and (3) radius of the fruit. For a fruit dropped on a hard, flat surface, the maximum internal shear stress (τ_{max}) is given by:

$$\tau_{max} = (Wh_1)^{1/5} E^{4/5} (1/R)^{3/5}$$

where:

W = weight of fruit
h_1 = drop height
E = elastic modulus of fruit
R = radius of fruit

Mohsenin (1978) extented the hertz contact theory for using drop tests of apples in order to determine the thickness of padding required using internal shear theory to predict bruising.

Using a different approach, Fluck and Ahmed (1973) studied impact damage using the effect of impulse-momentum, force and velocity on impact damage of fruits.

Another failure criterion using maximum strain for apple flesh had been proposed by Segarlind and Fabro (1978). These investigators hypothesized that failure in apple flesh occurs when a normal strain exceeds a critical value. Thus, to date, there have been many concepts proposed to explain the mechanics in impact failure in fruits but none have been proven completely satisfactory in a generalised form. In addition, the biological tissues are rheological in nature and cellular-nonhomogenious and nonisotropic. Failure in these materials depends upon the localized microstructure and state of stress.

Promising efforts at generalizing a failure criteria for apple tissue are discussed by Mittal et al. (1980) and Morrow (1980). While these studies are still being conducted, indications are that it is possible to develop a failure criteria which accounts for the viscoelastic nature of the tissue. Their work also permits investigation of incipience of failure under various modes of loading.

OBJECTIVES

Impact bruising is a limitation of applying mechanical harvesting to fresh market fruit. The mechanics of impact is neither well understood nor its relation to fruit maturity established.

This study was done to: (1) establish a relation between maturity and bruise volume for Red and Golden Delicious apples. (2) study the effect of firmness, diameter and energy on bruise volume.

MATERIALS AND METHODS

Sampling and Replication

Nine year old trees of Red Delicious and Golden Delicious apples on Malling 7 rootstock, growing at the University Plant Science Farm, Morgantown, WV, were used for this study. The bloom dates for Red Delicious and Golden Delicious were April 27 and May 3, respectively. Fruit from two trees of each variety with a comparable fruit load were sampled at approximately two week intervals starting in late July. Fruit sampling was continued, past optimum harvest time, until late October. At each sampling date ten apples were picked at random from each of the two Red Delicious and Golden Delicious trees and individual weight and diameter were recorded. Fruit firmness and impact tests were conducted on both the blushed and the unblushed sides of each fruit. This provided 40 observations on firmness and bruising for each variety at each sampling date.

Fruit Firmness Measurement

Firmness was measured using a 1.11 cm (7/16 in.) Magness Taylor probe mounted in Insron TM tester (fig. 1). The fruit was mounted on a wax ring. Two firmness values were recorded, one from each side of

FIG. 1. QUASI-STATIC FIRMNESS MEASUREMENT USING A 1.11 CM (7/16 IN.) MAGNESS TAYLOR PROBE

the fruit. A loading rate of 2.54 cm per minute was used and the force versus time curve was recorded on an XY recorder. The maximum recorded probe force was the firmness value.

Impact Testing

The impact apparatus shown in Fig. 2 and 3 was developed to measure rebound time by using an electronic counter in the time-interval mode (Diener *et al.* 1979). A quartz load cell located under the target plate started the counter operation. The counter displayed the total rebound time in milliseconds. By having the drop height and rebound height , the percent of energy lost due to impact could be calculated. In the present study, only bruise volume was measured as this parameter directly gives the bruise resistance. The fruit was held and released using a vacuum fixture. This served to reduce rotation of the fruit during free fall, fixed drop height, and locate the impact on the same position on the target.

At each sampling period the diameters of the fruit were averaged and the drop height was adjusted to keep an average height of 25.4 cm.

Two drops were made, one on opposite sides of the fruit. The apples were sectioned through the bruise and the depth, d, and surface diameter, D, was recorded (fig. 4). The bruise volume, V, was calculated using the relation for a partial sphere where:

$$V = (\pi/6)d[0.75 \ D^2 + d^2]$$

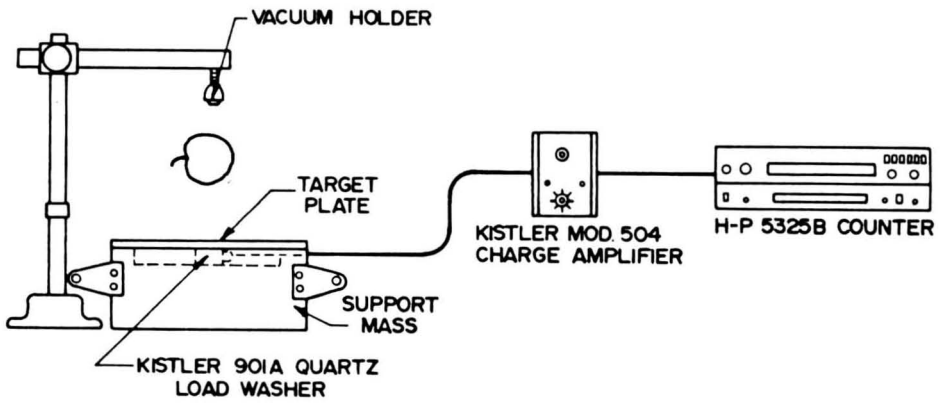FIG. 2. IMPACT TESTING USING A 25.4 cm CROP ON A FLAT STEEL PLATE

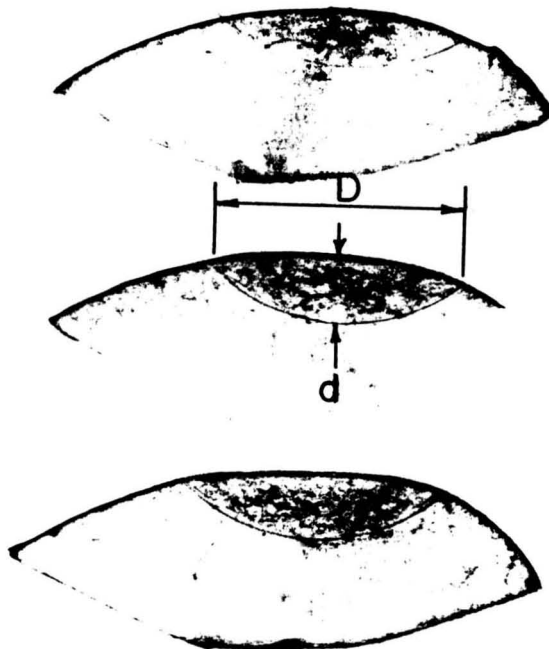FIG. 3. SCHEMATIC DRAWING OF APPARATUS USED FOR IMPACT TESTING

FIG. 4. SECTIONS OF APPLE SHOWING DIMENSIONS OF BRUISE VOLUME

RESULTS AND DISCUSSION

Firmness (Peak Probe Force)

Firmness as measured by peak probe force had a strong linear relationship with day after bloom (Fig. 5). Although both varieties started out at similar levels of firmness, Golden Delicious firmness decreased at nearly twice the rate (slope) of Red Delicious. These results are in agreement with most authors.

Bruise Volume (Constant Drop Height)

This study was concerned primarily with the bruise susceptibility as the fruit matured on the tree. Fruit thus would remain at constant height throughout the season until harvested. Factors such as texture, weight and size would determine the bruise volume resulting in the fruit. By maintaining a constant drop height in this study, the bruise volume in Fig. 6 gives a direct measure of the bruise susceptibility of the apple.

Bruise volume had a strong linear relation with day after bloom. It is apparent that apples should be harvested mechanically as early as possible to reduce damage. However, there is some indication that bruise volume does not change to any extent after 150 days past bloom. More frequent data points would need to be taken during this period of verification. Table 1 shows a slightly greater increase in weight for Golden Delicious which would increase impact energy for that variety. Table 1 also shows Golden Delicious to have a slightly greater diameter which, according to maximum shear theory, would reduce bruise volume. To study the effect of these parameters the effect of weight must be removed. This can be done by dividing the bruise volume by the energy input to obtain specific bruise volume which is discussed later.

Bruise Volume versus Impact Energy (Drop Height)

Bruise volume also related linearly with apple weight (impact energy) for both varieties over the test period of July to October (Fig. 7). The increase in impact energy was due only to increase in weight of the apple. Chen and Sun (1981) found the same relation for apples tested at the same stage of maturity where the impact was varied by changing the drop height of the impact weight. Similar results were obtained by Nelson and Mohsenin (1968) and Holt and Schoorl (1977).

It should be emphasized that the change in impact energy in this study occurred over the growing season of the fruit while possible
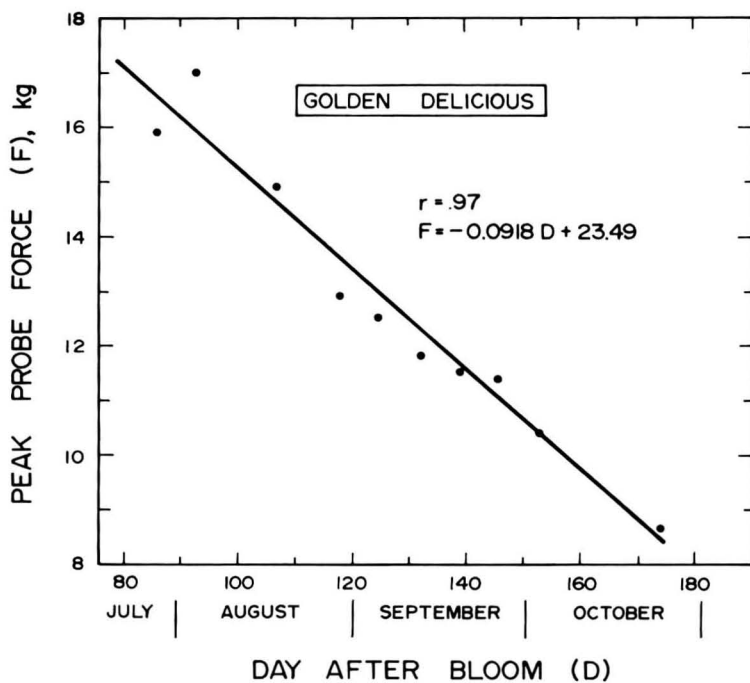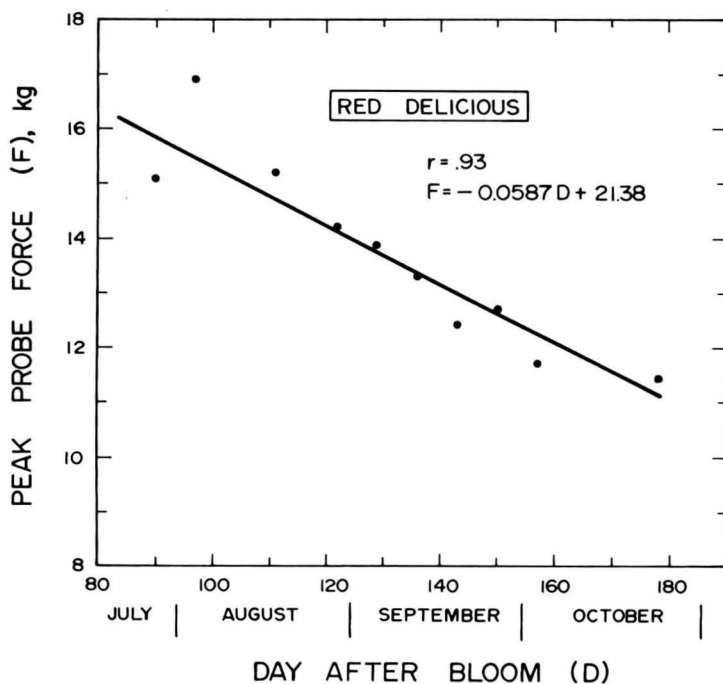
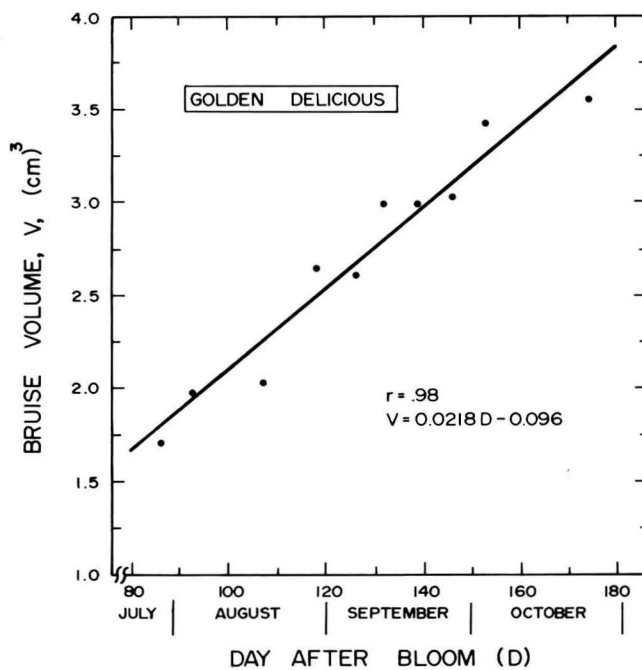FIG. 5. FIRMNESS VERSUS DAY AFTER BLOOM
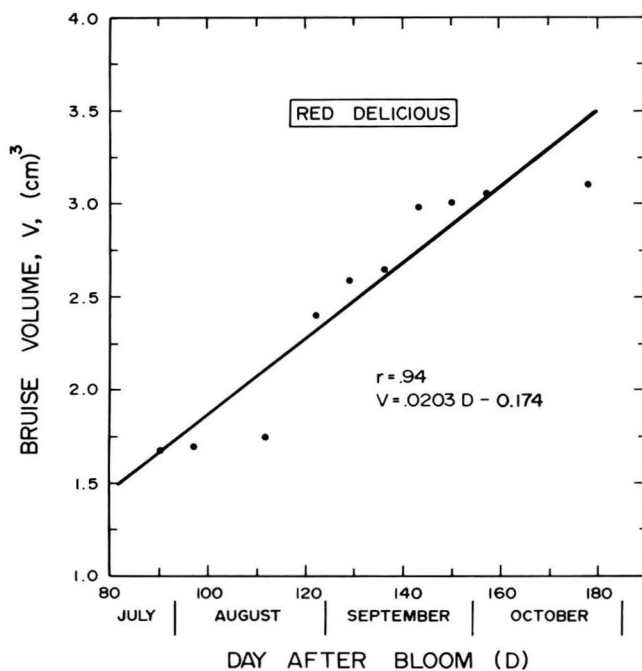
FIG. 6. BRUISE VOLUME VERSUS DAY AFTER BLOOM (Drop Height was held constant at 25.4 cm)
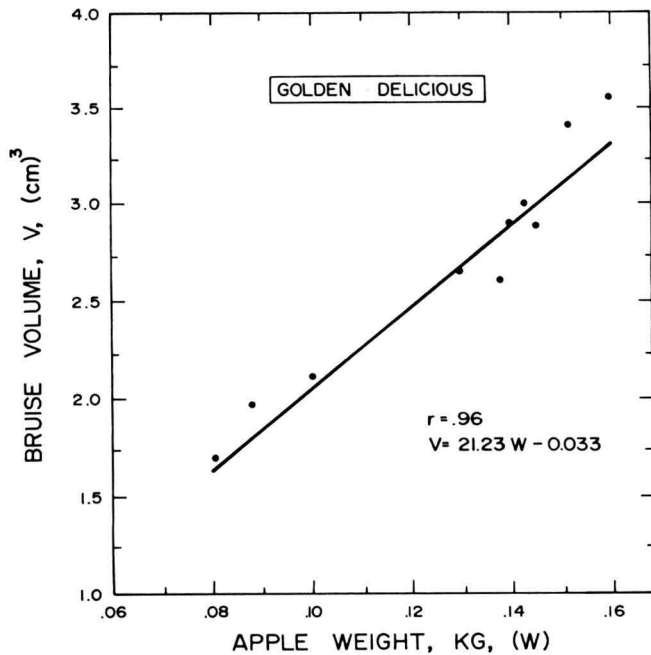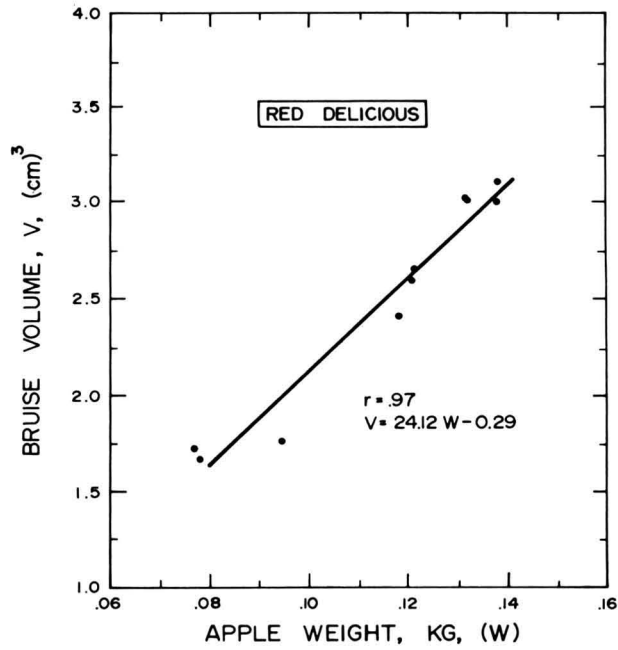
FIG. 7. BRUISE VOLUME VERSUS APPLE WEIGHT (ENERGY) (Data taken over test period July-October)

Table 1. parameters measured in bruise volume studies

Date	Bruise Volume (V) (cm³)	Specific Bruise Volume (V_s)	Firmness (F) kg	Fruit Diameter (cm)	Fruit Weight (kg)
		Red Delicious			
7-28	1.679	0.874	15.078	5.51	0.0784
8-4	1.712	0.894	16.870	5.56	0.0772
8-18	1.743	0.739	15.175	5.94	0.0948
8-29	2.405	0.811	14.192	6.39	0.1187
9-5	2.597	0.858	13.923	6.46	0.1218
9-12	2.652	0.872	13.327	6.56	0.1221
9-19	2.982	0.873	12.400	6.64	0.1382
9-26	3.014	0.907	12.753	6.77	0.1328
10-3	3.054	0.930	11.701	6.67	0.1322
10-24	3.113	0.903	11.438	6.85	0.1380
		Golden Delicious			
7-28	1.694	0.849	15.909	5.64	0.0812
8-4	1.960	0.928	17.057	5.85	0.0873
8-18	2.116	0.834	14.961	6.09	0.1017
8-29	2.648	0.815	12.919	6.74	0.1300
9-5	2.600	0.749	12.566	6.83	0.1382
9-12	2.895	0.841	11.729	6.80	0.1404
9-19	2.886	0.803	11.514	7.05	0.1447
9-26	3.032	0.843	11.404	7.05	0.1434
10-3	3.420	0.900	10.428	7.26	0.1515
10-24	3.544	0.886	8.698	7.38	0.1594

texture changes may also have occurred. The change in impact energy in studies by other authors were done by changing the impact mass for apples harvested on the same date.

Specific Bruise Volume

In order to remove the effect of fruit weight (impact energy) and variations in drop height, the bruise volume, V, was divided by the product of the weight, W, and the drop height, h. This gave a ratio of bruise volume per unit of energy impact of specific bruise volume, V_s, (Fig. 8).

Specific bruise volume both for Red and Golden Delicious apples was essentially the same over the season which indicates no change in susceptibility to bruise as the fruit matured. Red Delicious, however, showed a slight but non-significant increase in bruise susceptibility as the fruit matured.

R.G. DIENER, S.SINGHA AND J. PETIT
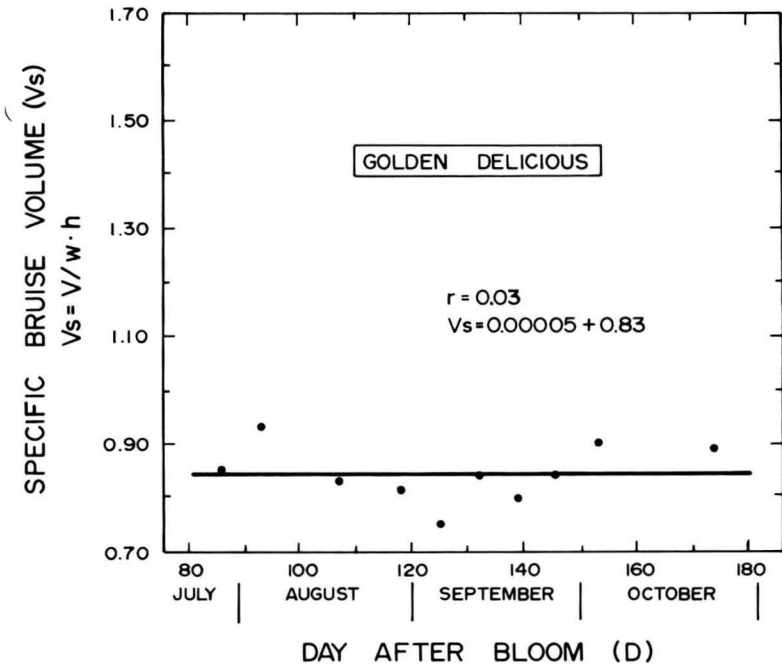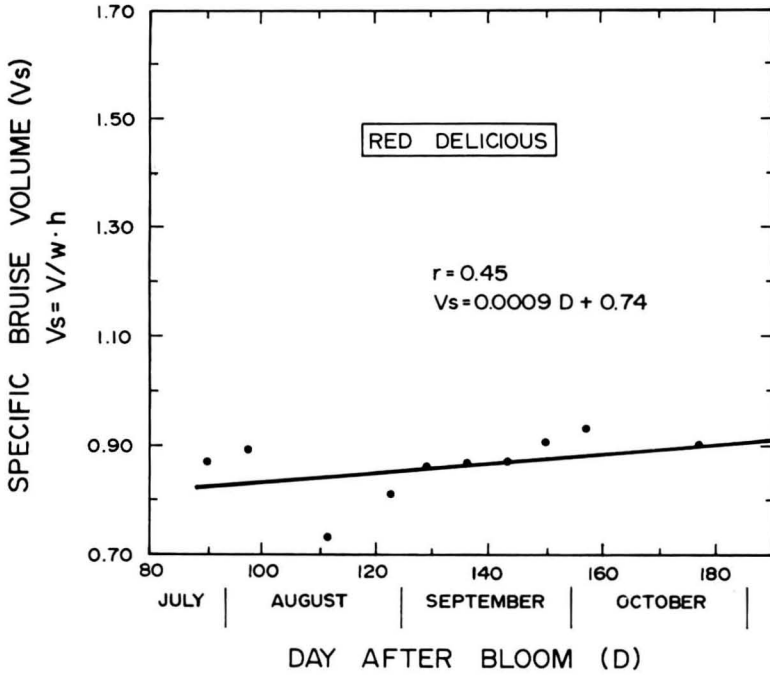
FIG. 8. SPECIFIC BRUISE VOLUME VERSUS DAY AFTER BLOOM

It should be noted that the above results are a combination of at least two effects which were not separated in this study. The first factor is the change in the susceptibility of the apple tissue at the interval level and the second factor concerns the change in diameter of the fruit. As the diameter increases, the impact surface becomes larger. The maximum shear theory predicts a decrease in internal shear in this case which would result in a decrease in bruising. This could make an increase in the bruise susceptibility of the fruit at the internal level.

However, the present study was designed to measure the overall bruising rather than these individual effects. The most important finding of this investigation is that the bruise susceptibility (specific bruise volume) is relatively constant over the season for the two varieties tested.

CONCLUSIONS

(1) Firmness of both Red and Golden Delicious varieties decreased in a linear relation with respect to day after bloom. The rate (slope) of decrease for Golden Delicious was about 70% higher than Red Delicious. (2) Bruise volume for whole apples dropped from a constant height increased in a significant linear relation with respect after bloom for both Red and Golden Delicious apples. The rate of increase (slope) was about 30% higher for Golden Delicious. (3) Bruise volume had a highly significant linear relationship with bruise energy (apple weight) measured over the growth period of the fruit. (4) Specific bruise volume (bruise volume per unit of energy input) did not change significantly over the growth period of the fruit.

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LITERATURE ABSTRACTS

ABSTRACTS FROM JOURNAL OF FOOD SCIENCE

Bentonite-Water Dispersions Simulated Foodservice Energy Consumption of Sausage Patties. N. Unklesbay, K. Unklesbay, D. Buergler, W. Stringer. J. Food Sci. *46*, 1808-1809 & 1816.

A research project was initiated to determine if bentonite-water dispersions could simulate energy consumption of two sizes of sausage patties during convective heat processing. Based on sausage patty composition, a mixture containing 18.2% bentonite and 81.8% water was used. Procedures simulated those reported for three different oven loads of sausage patties. Energy consumption was monitored throughout heat processing and was expressed as watt hours per oven load and per pan. No significant differences were found between sausage and bentonite patties for the energy consumption required for each oven load. For this food product, bentonite-water dispersions were found to be effective food models which could substantially reduce food costs for research activities.

Effect of Equilibrium Water Activity on the Bulk Properties of Selected Food Powders. R. Moreyra, M. Peleg. J. Food Sci. *46*, 1918-1922.

The bulk properties of powdered coffee creamer, infant formula, salt and sucrose at different levels of water activity were characterized by mechanical methods. These included loose bulk density, compressibility, cohesion, % irrecoverable work in compression and asymptotic modulus after stress relaxation. In the crystalline powders the physical characteristics generally followed the pattern established by the moisture content with an apparent critical water activity beyond which changes became drastic. In the creamer and formula which were very cohesive even in the dry form, the changes in bulk properties were generally more gradual. The rheological tests indicated that much of the physical changes in the salt and sucrose powders could be attributed to surface moisture. In the creamer and formula the plasticity of the particles material was also a major factor that affected the bulk behavior.

Temperature Dependence of Effective Diffusion Coefficient for Total Solids During Washing of Cheese Curd. J.A. Bressan, P.A. Carroad, R.L. Merson, W.L. Dunkley. J. Food Sci. *46*, 1958-1959.

The temperature dependence of the effective diffusion coefficient of total solids from small curd cottage cheese was estimated by fitting batch washing data at several temperatures (25°C, 35°C, 50°C, and 58°C) to a previously developed mass transfer model. The model was based on spherical geometry of curd particles. The correlation for diffusivity was found to be $D_{effective} = (0.0658\ T + 1.72) \times 10^{-6}$, where $D_{effective}$ is in cm^2/sec and T is in °C.

Water Vapor-Air Effective Diffusivity in Apple Tissues. P. Forebito, M.J. Urbicain, E. Rotstein. J. Food Sci. *46*, 1960-1961.

Water vapor-air effective diffusivity is one of the tranport properties needed for design, modeling, and simulation of many food processes. The effective diffusivity and a tissue structure factor are defined and determined by a method based on steady state countercurrent diffusion flux under zero pressure gradient. The diffusion cell is described and preliminary results are reported.

A Computerized Procedure for Estimating Chemical Changes in Thermal Process Systems. A.E. Labropoulos, A. Lopez, J.L. Baker. J. Food Sci. *46*, 1976-1977.

Chemical changes caused by heating in a continuous flow, helically coiled tube indirect UHT process system were evaluated and compared to a nonflow vat process system. A computerized procedure was developed to estimate the rates (R) and accumulated values (F_c) of chemical changes in the various stages of the UHT and vat thermal processes. The procedure could also be used to determine the conditions necessary to optimize quality and/or nutient retention. Data were based on 300°F and 3.3 sec holding time in the continuos process and 180°F for 30 min holding time in the vat system. Approximately 10% of the overall chemical changes occurred during the heating period for both processes, 88% and 87% during the holding periods, and 2% and 6% during the cooling respectively for the UHT and vat processes.

Water Activity Determination with the Proximity Equilibration Cell. T.D. McCune, K.W. Lang, M.P. Steinberg. J. Food Sci. *46*, 1978-1979.

The objective was to develop a new method for water activity (a_w) determination. A reference material (circle of filter paper) known sorption isotherm was equilibrated to the sample. Sorptions isotherm data for this paper were obtained by equilibrating for 24 hr to each of six salt slushes; these data were described well by a linear equation relating moisture content to $\log(1 - a_w)$. This equation served as the calibration curve. Results showed that this new method (1) does not require a vacuum, (2) gives a linear calibration equation, (3) is applicable over the a_w range from 0.40-0.98, and (4) with minor replication can bring the standard deviation of the mean to less than ± 0.01.

Water-Thawing of Fish Using Low Frequency Acoustics. A.D. Kissam, R.W. Nelson, J. Ngao, P. Hunter. J. Food Sci. *47*, 71-75.

Blocks of Pacific cod (plate frozen; 91-mm thickness and 12.7 kg) were thawed in an 18°C circulated water bath and simultaneously exposed to 1500 Hz acoustic energy not exceeding 60 watts. A ceramic transducer was positioned for light contact with a frozen block. A motorized belt moved the block in order to distribute the 239 cm^2 transducer over the 1500 cm^2 block surface. At 60 watts continuous input to the transducer, the block thawed in 71% less time than water-only controls. Quality analyses indicated that the flesh was not adversely affected by the acoustic waves.

Modeling of Isothermal Diffusion of Whey Components from Small Curd Cottage Cheese During Washing. J.A. Bressan, P.A. Carroad, R.L. Merson, W.L. Dunkley. J. Food Sci. 47, 84-88.

The batchwise washing of whey components from small curd cottage cheese is modeled as an isothermal diffusion process in a porous medium with several refinements to account for the whey on curd surfaces that is carried into the washing system. Three geometric approximations are considered. Apparent diffusion coefficients for total solids and lactose at 25°C are determined. Results show that diffusion from a spherical particle with consideration of whey entrained in curd interstices by capillary forces is an acceptable basis for mass transfer model.

Heat Transfer During the Washing of Small Curd Cottage Cheese.. J.A. Bressan, P.A. Carroad. J. Food Sci. 47, 89-91.

The heat transfer which occurs during the cooling of small curd cottage ceese during washing is mathematically modeled as a conduction process. The thermal diffusivity for curd was determined experimentally and shown to agree with predictions of correlations in the literature. Heat transfer occurs rapidly in curd, and is a relatively less significant design basis for washing systems than mass transfer.

Kinetics of Browning and Protein Quality Loss in Whey Powders During Steady State and Nonsteady State Storage Conditions. T.P. Labuza, M. Saltmarch. J. Food Sci. 47, 92-96 & 113.

Comparison was made between the amount of browning and protein quality loss during storage of whey powder under steady state conditions (25, 35 and 45°C and a_w's of 0.33, 0.44 and 0.65 at each temperature) and a fluctuating temperature condition of 25/45°C with alternating 5 day periods at each temperature. The results showed that the maximum rate of browning and loss of protein quality (e-DNP-lysine and RNV by Tetrahymena assay) occured at a_w 0.44 rather than at a higher a_w as is found for many dried foods. The Q_{10}'s for the reactions were about 5 and 3.7 respectively, for browning and protein quality loss. Of major importance was that storage losses at constant a_w, but under the fluctuating temperature condition, were significantly greater than at the mean temperature of 35°C. Using steady state data from the 25, 35 and 45°C conditions, the prediction of browning and protein quality losses for the fluctuating condition compared favorably ($\pm$ 10%) to actual losses, based on the simple Arrhenius relationship which indicates that temperature history does not significantly change reaction mechanisms.

Shape Characterization for a Simple Diffusion Analysis of Air Drying of Grains. C. Suarez, J. Chirife, P. Viollaz. J. Food Sci. 47, 97-100 & 157.

This work proposes a simple method to characterize which of the elemental geometries (slab, cylinder or sphere) would be a better approximation for the diffusion analysis of air drying of grains having "nonconventional shapes." The method is tested with experimental drying data obtained for soybeans, rough rice, wheat and peanuts.

Mass Balance Model for Enthalphy of Water Binding by a Mixture.
K.W. Lang, R.Mcl. Whitney, M.P. Steinberg. J. Food Sci. *47*, 110-113.

A thermodynamic approach was based on sorption data over a wide range of water activity (a_w) at each of three temperatures. The hypothesis tested was *the total partial enthalpy change for the water of a mixture is equal to the sum of the partial enthalpy changes for the water of the individual ingredients at the same a_w*. This was tested with sorption data for starch, casein, sucrose, starch:casein (1:1) and starch:sucrose (9:1) at 7.2, 20 and 30°C. Experimental values for the starch:casein mixture were in agreement (±5%) with those calculated from data on the individual ingredients, validating the hypothesis for a mixture of polymers. The starch:sucrose indicated a greater variation as the sucrose concentration increased to saturation.

Comparison of Optimization Techniques for Application to Food Product and Process Development. S. Nakai. J. Food Sci. *47*, 144-152 & 157.

The super-simplex optimization was modified by incorporating a quadratic regression subroutine. The new algorithm was found to be more efficient in converging at the optimum than the following algorithms: fractional factorial designs, sequential single-factor search, pattern-search method, Morgan-Deming simplex and super-simplex. The efficiency of the modified super-simplex optimization was dependent on the fitness of the regression equation to the model equation. Response surface analysis was accurate only when the model equation was quadratic factorial and the boundary covered the optimum. When a constraint was imposed to restrict the search within the boundary, unlike other simplex algorithms including the weighted centroid method, the modified super-simplex algorithm circumvented a problem of the search stalling at the boundary. Since it is not unusual for optimization to be restricted within boundaries, the modified super-simplex algorithm could be useful in optimizing food processing and analysis. When the modified super-simplex technique is applied to food research, even higher optimization efficiency could be expected by incorporating backward stepwise multiple regression analysis instead of the quadratic regression subroutine with regression equations of set formulae. To obtain a regression equation fit better to the true response surface, all information, including graphics, should be utilized.

Thermal Process Calculations for Different z and j_c values using a hand-held calculator. J. Kao, D. Naveh, I.J. Kopelman, I.J. Pflug. J. Food Sci. *47*, 193-197.

Equations facilitating the calculation of F_0 or process time used in the design and evaluation of thermal processes for low-acid foods packaged in hermetically sealed containers for j_c values of 0.4-2.3 and a z value of 10-26°F are presented. The relationships are based on the data presented by Hicks (1958) and Hayakawa (1970). The equations, although complex, can be efficiently used to calculate sterilization values and processing times using presently available programmable calculators. The equations were developed and tested so the maximum error in a calculated result will not be more than 5%.

Thermal Conductivity of White Bread During Convective Heat Processing. N. Unklesbay, K. Unklesbay, M. Nahaisi, G. Krause. J. Food Sci. *47*, 249-253 & 259.

Thermal conductivity values of white bread were determined during heat processing to provide information for analytical modeling required during the convective heat and mass transfer of the baking process. Selected physical properties of bread were determined: moisture, volume, bulk density and porosity. White bread was baked in a forced-air convection oven for 8, 16, 24 and 32 min. Thermal conductivity values ranged from 0.00072-0.00064 watts/cm-°C. Although a downward trend was observed and explained, no significant differences were revealed among thermal conductivity values. Thermal conductivity values were indirectly linearly dependent ($p<0.05$) on volume and porosity; directly, to bulk density and moisture loss.

Effect of Steam Temperature Speed of Cooling and Cutin Disruption in Steam and Lye Peeling of Apples. D.A. Smith, W.A. Dozier, W.A. Griffey, K.S. Rymal. J. Food Sci. *47*, 267-269.

A laboratory model steam peeler was adapted to accept superheated steam and direct injection of cold water in order to study the effect of rapid heating with superheated steam and rapid cooling under partial vacuum on the peeling efficiency of 'Red Delicious' apples. A test was also designed to determine the effect of physical disruption of the cuting layer on the efficiency of caustic peeling. Steam peeling resulted in higher peeled yields and brighter product color than caustic peeling. The peeled yields were 97.5% for superheated steam-peeled apples with flash cooling, 91.7% for caustic peeled fruit which had a prepeel treatment to physically disrupt the cuting layer, 85.8% for conventionally caustic-peeled fruit, and 82.7% for the mechanically peeled control.

Economic Comparison of Canning and Retort Pouch Systems. J.R. Williams, J.F. Steffe, J.R. Black. J. Food Sci. *47*, 284-290.

The economic feasibility of using the retort pouch for processing, packaging and distributing processed fruit and vegetable products during a period of rising energy prices was examined. A retort pouch packaging system was found to be the overall minimum cost packaging system among three packaging systems considered—an existing canning line, a new canning line, and a retort pouch line. Although the costs associated with acquiring and maintaining the durable machinery for retort pouch processing are significantly higher than for a new canning system or an existing canning system, other operating expenditures considered in the packaging systems are considerably lower. Lower freight costs, attributed to the lighter weight and smaller volume of pouches than cans, are the major contributors to the cost effectiveness of the retort pouch packaging system. Energy savings in processing the pouch versus the cans are of little significance, but the comparatively lower amount of energy used in transportation and container manufacture has an important role in the cost effectiveness of the retort pouch packaging system.

Energy Consumption in Water Blanching. T.R. Rumsey, E.P. Scott, P.A. Carroad. J. Food Sci. *47*, 295-298.

The energy consumption of a tubular water blancher and a water blancher with screw conveyor were measured as a basis for suggesting energy conserving modifications. The former required 0.54 MJ/kg and the latter 0.91 MJ/kg, indicating the importance of complete steam condensation. A pilot scale experiment with a water blancher heated with heat exchange and by steam injection confirmed the energy savings potential of heating with an exchanger to minimize escape of steam rather than by steam injection.

Freezing-Thaw Stability of Illinois Soybean Beverage. S.W. Yeh, L.S. Wei, A.I. Nelson, M.P. Steinberg. J. Food Sci. *47*, 299-302.

The objective of this work was to study the effects of freezing conditions, processing and formulation variables on freeze-thaw (F-T) stability of Illinois soybean beverage. Objective and subjective evaluations were made on a sample before and after freezing. Total solids content of the supernatant from a centrifuged sample was used to calculate a F-T stability index. This index was below 35% for both plain base and plain beverage. The freeze-thaw stability was affected by freezing temperature, holding time before freezing, changing of temperature during frozen storage and desludging. However, length of frozen storage and homogenization pressure had no apparent effect. Addition of sugars and salt resulted in a beneficial effect on the stability. In order to prevent visible freeze damage, approximately 7% sucrose or 5% dextrose hydrate were required in a beverage containing 0.2% salt.

Processing Retort Pouches in Conventional Sterilizers. R.A. Roop, P.E. Nelson. J. Food Sci. *47*, 303-305.

A cylindrical rack was designed to hold four 130 mm × 178 mm retortable pouches. The outer dimensions of the cylinder were 157 mm × 178 mm, identical to a No. 10 can. These dimensions permitted pouch processing in traditional sterilizers that accept cans of this size. Dimensional considerations, pouch orientation, and heat distribution were tested in 100% steam. This racking method was found to provide equal heat treatments to all pouches regardless of horizontal, vertical or rolling orientations. These results suggest the use of various conventional sterilizers for pouch processing with little or no modification.

A Monolayer for Use in Sorption Studies. M. Caurie. J. Food Sci. *47*, 332-333.

It has been indicated that because of the assumption that $E_2 = E_L$ used in its derivation the H.E.T. infinite layer equation cannot describe adsorption beyond the first adsorbed layer. A simplification of the three constant B.E.T. equation provides a new monolayer equation which agrees more with the above assumption, from which the Langmuir equation is shown to arise as a special case at low pressures. The monolayer capacity predicted by the new monolayer equation appears to maintain a more stable product than is possible with the classical B.E.T. infinite layer equation. The use of the new equation in sorption studies is recommended.

Storage Stability of Orange Juice Concentrates Package Aseptically.

J. Kanner, J. Fishbein, P. Shalom, S. Harel, I. Ben-Gera. J. Food Sci. 47, 429-431 & 436.

Orange juice concentrates were packaged aseptically by a "Dole" aseptic canning machine using 6 oz metal cans. The final juke products (11°, 34°, 44°, 58° Brix) were stored between −18° and 36°C and tested periodically for nonenzymatic browning, ascorbic acid destruction, furfural and sensory changes. Nonenzymatic browning, the main deterioration phenomena in these products, was satisfactorily retarded at 12°C or lower. Ascorbic acid destruction rate constant was dependent on temperatures between 5 and 25°C, and was affected by degree of juice concentration. Furfural accumulation in juice was higher than that in 58° Brix concentrate. Orange juice concentrate of 58° Brix did not show flavor changes after storage at 5°C or 12°C for 17 or 10 months, respectively, when evaluated after reconstitution to 11° Brix.

Dehydrated Blueberries by the Continuous Explosion-Puffing Process.

J.F. Sullivan, J.C. Craig, Jr., E.D. Dekazos, S.M. Leiby, R.P. Konstance. J. Food Sci. 47, 445-448.

A blueberry dehydration process which includes the unique continuous explosion-puffing system (CEPS) is described. A drying study including alternate drying pretreatments failed to increase the dehydration rate. It was found that care during processing was necessary to prevent rupture of the berries as rupture caused bleeding during drying which reduced the drying rate. Optimum operating conditions for CEPS were established for blueberries. Measurements of dried blueberry properties such as bulk density, color, rehydration, and disintegration were used to determine optimum operating conditions for pressure (103 kPa), temperature (190°C), and food moisture (18.5%) for CEPS.

Descriptors for Texture Profile Analysis of Frankfurter-Type Products from Minced Fish.

P.M. Arocha, R.T. Toledo. J. Food Sci. 47, 695-698.

The texture profile of frankfurter-type products prepared from minced Spanish mackerel (*Scomberomorus maculatus*) was evaluated. Twelve character notes were identified: springiness, hardness, cohesiveness, moisture release, crumbliness, coarseness, graininess, juiciness, adhesiveness, lumpiness, chewiness, and mouthfeel-oiliness. Overall texture acceptability was also evaluated. Differences in juiciness and mouthfeel-oiliness were not detected. Springiness, hardness, cohesiveness, and lumpiness had the highest correlation with the overall texture acceptability. Products with 10% soy protein fiber (SPF) were better accepted than those having 20% or no SPF. Egg white (to 20%) improved the texture; however, its flavor was detectable when 10% or more was added. The most acceptable texture was exhibited by products containing 5-10% ground drum-dried fish.

Kinetics of Ascorbic Acid Autoxidation as a Function of Dissolved Oxygen Concentration on Temperature.

M.H. Eison-Perchonok, T.W. Downes, J. Food Sci. 47, 765-767 & 773.

The kinetics of ascorbic acid autoxidation was studied at pH 6.1 ($\mu = 0.08$) using a buffered model system. Oxygen replenishment in the solution was accomplished by shaking the reaction vessel in a shaker water bath or by bubbling oxygen-nitrogen

gas mixtures through the solution. Using the former system, a second order rate constant of 58.19 ± 11.92 $min^{-1}M^{-1}$ was calculated (45°C). Since the shaker bath did not assure oxygen replenishment and dissolved oxygen levels could not be varied, the latter system was developed. The second order rate constants in the gas mixture experiments ranged from 20.80 ± 2.28 $min^{-1}M^{-1}$ (30°C) to 176 ± 6.93 $min^{-1}M^{-1}$ (55°C). Activation energies measured under different conditions ranged from 9.47 to 16.43 kcal $mole^{-1}$.

Rheological Properties of Two Heat-Induced Protein Gels. D.W. Hickson, C.W. Dill, R.G. Morgan, V.E. Seat, D.A. Suter, Z.L. Carpenter. J. Food Sci. *47*, 783-785 & 791.

Rhelogical properties of heat-induced gels from egg albumen and bovine plasma proteins were measured using a mechanical loading device. Each protein was tested at 8% protein concentration and heated for 0-120 min. at 80°C in an agitating water bath. After heating, the viscosity index, apparent elasticity and initial penetration force of the gels were evaluated. Bovine plasma protein dispersions exhibited a substantially higher viscosity index, apparent elasticity and initial penetration force than egg albumen gels. Bovine plasma proteins produced a gel structure which was strong and elastic. By comparison, heat-induced gels of egg albumen proteins were fragile and somewhat brittle.

Combining Process Variables and Ingredient Components in Mixing Experiments. J.A. Cornell, J.C. Dung. J. Food Sci. *47*, 836-843 & 848.

This paper reviews the use of statistical designs formed by combining simplex-centroid designs in the ingredient or mixture components with factorial arrangements in the process variables. Three data sets are presented from a fish patty experiment in which three fish species (mullet, sheepshead, and croaker) were blended and the patties were prepared according to the settings of three process variables (oven cooking temperature, oven cooking time, and deep fat frying time). The response values are the average overall acceptance ratings of the patties and the average texture rating of the patties. Detailed steps in the data analysis are provided to illustrate the techniques that are used and the type of information that is acquired from experiments containing mixture components and process variables.

Effects of Food Composition, pH, and Copper on the Degradation of Vitamin A in Beef Liver Puree During Heat Processing. S.A. Wilkinson, M.D. Earle, A.C. Cleland. J. Food Sci. *47*, 844-848.

Kinetics of the loss on heating of vitamin A (measured as transretinol) were determined in liver and fat mixtures. Five variables (fat, protein and moisture contents, copper concentration, and pH) were studied in a two-stage experimental design. Steady-state heating, in small tubes at three different temperatures (102°, 112°, 122°C) for times up to 400 min was used to determine order of reaction, rate constants, and temperature dependence of the rate of loss of vitamin A. The rate followed apparent first order kinetics and the Arrhenius relationship explained its

temperature dependence. Significant factors affecting rate were moisture content and copper. Activation energy ranged from 36-122 kJ/mol with changes in composition.

Comparisons of the General and Ball Formula Methods for Retort Pouch Process Calculations.. S.H. Spinak, R.C. Wiley. J. Food Sci. 47, 880-884 & 888.

Comparisons of general and formula methods were made for pouches processed underwater in a still vertical retort. Changes were considered in the conventional use of the formula method. Heat penetration tests were performed using horizontally positioned pouches (3/4 inch pouch thickness). Tests on pureed product using a common brass thermocouple receptacle indicated a probatility of less than 1% that errors were caused by the receptacle. Tests were then conducted using the same puree and two types of particulate products.

Ultrafiltration and Reverse Osmosis Recovery of Limonene from Citrus Processing Waste Steams. R.J. Breaddock. J. Food Sci. 47, 946-948.

Commercial ultrafiltrations (UF) and reverse osmosis (RO) membranes were used to concentrate the terpene, limosene, present in cold pressed oil centrifuge effluent and molasses evaporator condensate. UF membrane rejections were 78-97% for mixtures with initial limoneme concentrations from 0.04-0.6% v/v. RO membrane rejection of limonene ranged from 87-99% for feed streams containing 0.06-0.23% limonene. Initial membrane flux rates for centrifuge effluents were in the range 10-100 kg/m²/hr. Evaporator condensate fluxes were higher, 25-400, while pure water rates ranged from 25 (RO) to 1000 kg/m²/hr (UF). Contact with limonene adversely affected membrane flux rates in decreasing order of severity: polysulfone > cellulose acetate > teflon-type.

Behavior of Low Molecular Weight Organic Acids During Freeze Drying. L. Gero, T.G. Smyrl. J. Food Sci. 47, 954-957.

The retentions of several low molecular weight organic acids (formic-acetic, propionic, lactic, n-butyric and isobutyric) were measured during the freeze drying of model solutions in which dextran was employed as the dissolved solid. Acid retentions were found to increase with initial dextran content and with a decreasing rate of sample freezing. An increase in initial acid concentration was found to decrease the percent acid retained. Sample layer thickness and the presence of additional volatiles (ethanol and hexanol) were found to have very little influence on the degree of acid retentions.

Correction Factors for Non-Destructive Measurement of Residual Volume of Air in Retort Pouches. A. Ghosh, S.S.H. Rizvi. J. Food Sci. 47, 969-971.

A destructive and a nondestructive method of estimating residual volume of air in retort pouches were compared. The difference between the volumes of air given by two techniques were found to be significant ($P < 0.05$) by paired t-test. An indierct

calculation method was developed for estimation of internal pressure at neutrual bouyancy and when used in conjunction with Archimedes' Principle and Boyle's Law significantly improved the results. This method of calculating residual air in flexible pouches did not show any significant difference ($P > 0.01$) when compared to the standard destructive techniques. The procedure outlined is easy to use.

A Pilot-Plant Study of Continuous Ultrasonic Extraction of Soybean Protein. K.J. Moulton, L.C. Wang. J. Food Sci. 47, 1127-1129 & 1139.

Methods were studied to extract soybean proteins from commercial defatted flakes with ultrasonic energy, continuously and efficiently, in a pilot plant. Studies also included batchwise sonication of aqueous soybean slurries in a tank. Parameters investigated included soybean-to-solvent ratios of 1:10, 1:20, and 1:30; solvents of tap water and 0.1N NaOH; and extraction with and without sonication. Protein yield and energy requirements for extraction were measured to correlate the operating condition with the extent of protein extraction. For a residence time of 0.7 sec in the continuous sonication process, the extracted protein yield was greatest at 1:30 soy-to-alkaline solvent ratio. Energy input to produce protein isolate is the least at 1:10 soy-to-alkaline solvent. Although the continuous sonication procedure is workable, the commercial operation remains to be tested.

Effect of Trace Mineral Fortification on the Storage Stability of Ascorbic Acid in a Dehydrated Model Food System. D.B. Dennison, J.R. Kirk. J. Food Sci. 47, 1198-1200 & 1217.

The catalytic influence of the transition metals, iron, copper and zinc, on the storage stability of ascorbic acid in a dehydrated model food system was studied as a function of water activity (a_w). No catalysis by the added metals was observed at 0.10 and 0.40 a_w. This is interpreted as a lack of metal ion mobility and/or insolubility at low a_w, thus hindering the participation of the metals as catalysts. At 0.65 a_w, which is in the capillary region on the adsorption isotherm, a 2-4 fold increase in the rate of ascorbic acid destruction was observed in the presence of the trace minerals. The increased rate of ascorbic acid degradation at a_w 0.68 is believed to be the result of greater mobility of metal ions.

A Simplified Model for Freezing Time Calculations in Foods. R.H. Mascheroni, A. Calvelo. J. Food Sci. 47, 1201-1207.

A model is proposed for freezing time calculations which combines Plank's equation with the unsteady heat transfer solutions for the cooling of a slab of constant properties through the addition of precooling, change of phase and tempering periods. The change of thermal properties with the ice content is taken into account by proposing average values for the different periods. No adjustable parameters are used in developing the model. Results are compared for the case of beef freezing with those obtained numerically by using a heat transfer model with simultaneous change of phase and with experimental measurements showing good agreement.

Sorption/Desorption of VCM in PVC Selected Food Simulants Systems. M. Kontominas, J. Miltz, S.G. Gilbert. J. Food Sci. *47*, 1208-1210.

Sorption/desorption studies of VCM in the systems PVC/VCM/water, PVC/VCM/corn oil and PVC/VCM/heptane were carried out. At low VCM concentrations, classical curves are obtained, where the sorption isotherms are located below their desorption counterparts. Above a certain VCM concentration a crossover exists and an inversion of the curves occurs. It was suggested that the intersection between the curves represents the point where all the active sites in the polymeric matrix are occupied by monomer molecules. The negative values of the total Gibb's free energy and the energy of mixing in the polymer were found to increase with the decrease in monomer concentration pointing to the possibility that at low enough monomer concentrations no migration of VCM into the contained food from a PVC package may occur.

Mathematical Models for Nonsymmetric Freezing of Beef. A. DeMichelis, A. Calvelo. J. Food Sci. *47*, 1211-1217.

A microscopic balance with simultaneous change of phase together with equations for predicting the thermal properties as a function of the ice content and a cryoscopic descent model are used to simulate the nonsymmetric freezing of a beef slab. The equations are solved numerically to obtain temperature profiles as well as freezing times. Comparison with experimental results shows good agreement. A variation of the thermal center position throughout the freezing process is detected and assumptions to predict its position in the different periods of freezing are supplied. On the basis of these assumptions a simplified model for calculating processing times in plate freezers is proposed, showing good agreement with experimental freezing times and with predictions obtained from the numerical model.

Diffusional Behavior of Tripalmitin in Freeze-Dried Model System at Different Water Activities. W. Maesen, G. Bresseleers, P. Tobback. J. Food Sci. *47*, 1245-1249.

The diffusional behavior of tripalmitin (TP) in a low moisture model system composed of microcrystalline cellulose and gum arabic was found to be very dependent on the water activity (a_w), the temperature and the presence of paraffin oil (PO). The complex mechanism of mobilization of food components in dry systems, particularly that of TP in our system, has been discussed in detail. Such knowledge is especially important in relation to the reactions that occur in foodstuffs during dehydration and subsequent storage. As a typical example, the results on TP diffusion indicate that the restriction of enzymatic activity in dry systems may not solely be due to the diffusional limitations of the reactants.

Relationship between Static Electrical Conductivity and Unfrozen Water Content in Food Products. T. Hori, M. Kako, H. Hayashi. J. Food Sci. *47*, 1254-1256.

The static electrical conductivity measurements on frozen foods such as citrus juice and varieties of cheese showed that both conductivity and unfrozen water content in food products varied directly with temperature. In describing the log σ vs $1/T$ curve, where σ is the conductivity and T is the absolute temperature, it was found that the linear portion of the curves at low temperature was related to bound water content which was independent of temperature, whereas the non-linear portion in the temperature range between the freezing point and 10 or 35 degrees below the freezing point was related to the unfrozen free water content which was dependent on temperature.

Sorption Isotherms and Drying Rates for Mullet Fillet and Roe. K.V. Chau, J.J. Heinis, M. Perez. J. Food Sci. *47*, 1318-1322 & 1328.

Desorption isotherms at 25°C and 43°C and adsorption isotherms at 25°C were determined for salted and unsalted female roe of mullet (*Mugil cephalus*). Isotherms for ground white muscle of mullet were also determined for desorption at 25°C, 43°C, and 54.5°C, and for adsorption at 25°C. Adsorption-desorption hysteresis was evident for the sigmoid shaped isotherms. At 45°C and 15% RH, and also at 45°C and 25% RH, mullet fillets dry almost four times faster than mullet roe. An air temperature lower than 45°C should be used to obtain an acceptable color for the roe.

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HASSON, E. P. and LATIES, G. G. 1976. Separation and characterization of potato lipid acylhydrolases. Plant Physiol. *57*, 142—147.

ZABORSKY, O. 1973. *Immobilized Enzymes*, pp. 28—46, CRC Press, Cleveland, Ohio.

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