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ANALYSIS OF KINETICS OF QUALITY CHANGE IN FROZEN FOODS[1]

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ABSTRACT

Temperature fluctuations of frozen foods are of influence on frozen food quality. Prediction of quality changes under temperature fluctuations is therefore important in assuring high product quality and, by optimizing storage temperature, in conserving energy. This study is focused on applying kinetic models in analyzing Time-Temperature-Tolerance (TTT) data for frozen food storage and investigating the potential for use of kinetic parameters to describe quality degradation in frozen foods.

Based on theoretical considerations, quality life and activation energy are related by the equation:

$$\ln t_Q = \ln B + \frac{Ea}{R} \cdot \frac{1}{T}$$

where B is a function of the pre-exponential of Arrhenius equation, initial and end point quality magnitude.

Reasons for some TTT data to deviate from this relationship are:

A. Different standards for measuring quality lives of different storage temperatures or experiments.
B. Negative effect of temperature.
C. Variations in initial or final quality magnitudes for a given experiment.
D. Variations in packaging material and other factors influencing the quality magnitude or mode.

TTT experiments are suitable approaches for obtaining activation energy constants, although they are not applicable for determination of

[1] Presented at Summer Meeting of American Institute of Chemical Engineers in Detroit, Michigan on August 18, 1981. The authors—Dar-Jen Lai, Graduate Research Assistant and Dennis R. Heldman, Professor of Food Engineering, Michigan State University. Michigan Agricultural Experiment Station Journal Article No. *10400*.

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reaction order and rate constant. When dealing with overall quality life of several contributing factors, quality life for each component is needed to get a better description. Quality changes in terms of fraction of initial quality magnitude retained can be described by quality life, activation energy, temperature history and the constant, $\alpha = C_{tQ}/C_0$.

INTRODUCTION

Temperature fluctuations during storage and distribution of frozen foods are unavoidable. These fluctuations influence the rate of quality degradation and may result in visible loss of product quality. Predicting or describing quality change as influenced by temperature fluctuations is of importance in assuring high product quality. In addition, these predictions form the basis for making process evaluations such as determining which portion of the distribution chain is most detrimental to product quality. The opportunities for using higher storage temperatures for some food commodities need investigation in light of energy conservation concerns.

Early investigations on quality degradation of frozen foods, often referred to as time-temperature-tolerance (TTT) investigations, have provided significant amounts of information on the relationships among quality, time and temperature of various products. However, data from different authors may differ in the manner of describing or judging overall quality. Thus, in most cases, these data are not adaptable for practical prediction of quality degradation.

The investigation being reported analyzes TTT data using kinetic models and discusses the potential for using kinetic parameters to describe quality degradation of frozen foods. In addition, the purpose of this analysis is to develop and present procedures for collecting and using kinetic parameters for prediction of quality change in frozen foods during storage and distribution.

THEORETICAL CONSIDERATIONS

Time-temperature tolerance investigations for frozen foods were vigorously investigated in the 1950's and the 1960's. Generally, the data can be divided into two distinct groups. The analysis considerations were slightly different as will be described.

I. Analysis of Reaction Order and Rate Constant

Data from objective measurement of a specific characteristic or component related to food quality.

These data provide information on characteristic (or component) magnitude change as a function of time and temperature. Reaction order and rate constant with respect to this characteristic can be obtained from this type of data. Since only the characteristic of interest is monitored, the kinetic information obtained does not describe the deterioration reaction rate, even for the specific characteristic being monitored. Consider the general form of rate equation:

$$\text{Rate} - \frac{dX}{dt} = k[C_1]^{n_1}[C_2]^{n_2} \cdots$$

where $c_1, c_2, \ldots$ are magnitudes of components related to reaction rate. If C_1 is the only characteristic being monitored, then only under the conditions that the reaction is zero order, i.e.,

$$\text{Rate} = \frac{dX}{dt} = k$$

or the reaction rate is related to C_1 only, i.e.,

$$\text{Rate} = \frac{dX}{dt} = k[C_1]^n$$

can the analysis be straightforward. In most cases, TTT data can not be used to determine whether the overall deterioration reaction is zero order or the rate is related to C_1 only.

If there are other characteristics or components related to reaction rate, then analysis with respect to C_1 will, at best, give a pseudo-reaction order and pseudo-reaction rate constant. When other related characteristic or component magnitudes $[C_2], [C_3] \cdots$ are large in comparison with $[C_1]$, then, $[C_2][C_3] \cdots$ can be viewed as constant throughout the reaction, and,

$$\begin{aligned}\text{Rate} &= k[C_1]^{n_1}[C_2]^{n_2}[C_3]^{n_3} \cdots \\ &= k[C_{1,0} - X]^{n_1}[C_{2,0} - X]^{n_2}[C_{3,0} - X]^{n_3} \cdots \\ &\quad k[C_{1,0} - X]^{n_1}[C_{2,0}]^{n_2}[C_{3,0}]^{n_3} \cdots = k'[C_1]^{n_1}\end{aligned}$$

where $K' = k[C_{2,0}]^{n_2}[C_{3,0}]^{n_3} \cdots$

The pseudo-reaction order and rate constant are useful only under the conditions that the magnitudes of $[C_2], [C_3] \cdots$ are large and do not change significantly from one experiment to another.

Data from subjective tests.

These data provide information on the time required for frozen food quality to change in comparison to a controlled sample, i.e., high quality life (HQL), or the time required for a frozen food to be considered unacceptable for consumption, i.e., practical storage life (PSL). Most TTT data describe quality change in terms of these quality parameters. It is even more difficult to obtain a reaction order or a rate constant from these data.

Approximation method for determination of reaction rate constant.

Due to the complexity of the quality deterioration reaction, assumptions are needed to obtain approximate description of reaction rates.

a. Relationships between initial quality nagnitude (C_0) and end-point (of HQL or PSL) quality magnitude (C_{tQ})

There are three possible relationships between $[C_0]$ and $[C_{tQ}]$:

i. $[C_{tQ}]$ is independent of $[C_0]$, and is expected to be constant for an experiment. PSL by definition is most likely belonging to this type of relationship.

ii. $[C_0] - [C_{tQ}]$ is expected to be constant for an experiment. HQL by definition is assumed to follow this kind of relationship.

iii. $[C_{tQ}]/[C_0]$ is constant. For an experiment, it is usually expected to keep $[C_0]$'s constant. Therefore, either case (i) or (ii) can be expressed as $[C_{tQ}]/[C_0] = \alpha$ (a constant).

For different experiments, due to lack of absolute quantitative definition of overall quality, it is difficult to maintain either $[C_0]$'s or $[C_{tQ}]$'s at constant levels.

b. Zero order assumption and zero order reaction rate constant

The reaction rate for frozen food quality deterioration is small in most cases. Van Arsdel *et al.* (1969) therefore proposed a linear relation or zero order reaction for defining the deterioration reaction rate as:

$$\text{Rate} = \frac{1}{\text{HQL (or PSL)}}$$

If the assumption of zero order reaction is kept, then

$$\text{Rate} = \frac{dX}{dt} = k_0$$

$$[C_0] - [C_{tQ}] = X = k_0 \cdot t_Q$$

where t_Q = HQL (or PSL) in days. By incorporating

$$\frac{[C_{tQ}]}{[C_0]} = \alpha \tag{1}$$

then

$$[C_0] - [C_0] = k_0 \cdot t_Q$$

$$k_0 = \frac{(1 - a)[C_0]}{t_Q}$$

c. First order assumption and first order reaction rate constant

As in many cases, quality deterioration of frozen foods is assumed to follow the first order reaction rate. For a first order reaction with respect to overall quality magnitude,

$$\text{Rate} = \frac{dX}{dt} = k_1[C] = k_1[C_0 - X]$$

$$\ln \frac{[C_{tQ}]}{[C_0]} = -k_1 t_Q \tag{2}$$

or

$$k_1 = \frac{1}{t_Q} \ln \frac{[C]}{[C_{tQ}]}$$

Again, from equation (1)

$$k_1 = \frac{-\ln \alpha}{t_Q} \tag{4}$$

d. The characteristic of α

As described earlier, it is difficult to maintain either $[C_0]$'s or $[C_{tQ}]$'s constant for different experiments. Therefore, α is not constant for different experiments. In practical applications, it has to be evaluated from each individual case.

II. Analysis of Activation Energy

Considering a chemical reaction for deterioration:

a. if the reaction follows a first order rate, the rate of reaction can be expressed as Eq. (2):
Assuming the Arrhenius law is applicable, i.e.,

$$k = A \exp\left(\frac{-Ea}{RT}\right) \tag{5}$$

and substituted by Eq. (3), then:

$$\frac{1}{t_Q}\ln\frac{[C_0]}{[C_{tQ}]} = A\exp\left(\frac{-Ea}{RT}\right) \qquad \ln t_Q = \ln\frac{\ln\frac{[C_0]}{[C_{tQ}]}}{A} + \frac{Ea}{R}\cdot\frac{1}{T}$$

$$\text{let } B = \frac{\ln\frac{[C_0]}{[C_{tQ}]}}{A} \qquad \ln t_Q = \ln B + \frac{Ea}{R}\cdot\frac{1}{T}$$

b. if the reaction follows nth ($n \neq 1$) order reaction rate with respect to a specific component, the rate of reaction can be expressed as:

$$\begin{aligned} Rate &= \frac{dX}{dt} = k[C]^n \\ &= k[C_0 - X]^n \\ \frac{dX}{[C_0 - X]^n} &= kdt \\ \frac{1}{n-1}\left(\frac{1}{[C_t]^{n-1}} - \frac{1}{[C_0]^{n-1}}\right) &= kt \\ k &= \frac{1}{t_Q}\cdot\frac{1}{n-1}\left(\frac{1}{[C_{tQ}]^{n-1}} - \frac{1}{[C_0]^{n-1}}\right) \end{aligned}$$

from Eq. (5),

$$\frac{1}{t_Q}\cdot\frac{1}{n-1}\left(\frac{1}{[C_{tQ}]^{n-1}} - \frac{1}{[C_0]^{n-1}}\right) = A\exp\frac{-Ea}{RT}$$

$$\ln t_Q = \ln\frac{[C_0]^{n-1} - [C_{tQ}]^{n-1}}{(n-1)([C_0]^{n-1}\cdot[C_{tQ}]^{n-1})A} + \frac{Ea}{R}\cdot\frac{1}{T}$$

$$let\ B = \frac{[C_0]^{n-1} - [C_{tQ}]^{n-1}}{(n-1)([C_0]^{n-1}\cdot[C_{tQ}]^{n-1})A}$$

$$\ln t_Q = \ln B + \frac{Ea}{R}\cdot\frac{1}{T}$$

c. if the reaction follows 2nd order reaction rate with respect to two components C and D, the rate of reaction can be expressed as:

$$Rate = \frac{dX}{dt} = k[C][D]$$

$$= k[C_0 - X][D_0 - X]$$

$$\frac{dX}{[C_0 - X][D_0 - X]} = kdt$$

$$\frac{1}{[C_0] - [D_0]} \ln \frac{[D_0][C_{tQ}]}{[C_0][D_{tQ}]} = kt$$

from Eq. (5),

$$\frac{1}{t_Q} \frac{1}{([C_0] - [D_0])} \ln\left(\frac{[D_0][C_{tQ}]}{[C_0][D_{tQ}]}\right) = A \exp \frac{-Ea}{RT}$$

$$\ln t_Q = \ln\left(\frac{\ln \dfrac{[D_0][C_{tQ}]}{[C_0][D_{tQ}]}}{A([C_0] - [D_0])}\right) + \frac{Ea}{R} \cdot \frac{1}{T}$$

$$\ln t_Q = \ln B + \frac{Ea}{R} \cdot \frac{1}{T}$$

where

$$B = \frac{\ln \dfrac{[D_0][C_{tQ}]}{[C_0][D_{tQ}]}}{A([C_0] - [D_0])}$$

The relationship between quality life and absolute temperature is therefore represented in the general form of:

$$\ln t_Q = \ln B + \frac{Ea}{R} \cdot \frac{1}{T} \tag{6}$$

where B is a function of related initial quality magnitude ($[C_0], [D_0]$), end point (of quality life) quality magnitude ($[C_{tQ}], [D_{tQ}]$) and the pre-exponential (A) in Arrhenius equation.

Since there is no absolute quantitative definition for overall quality magnitude, it is not plausible to expect data from different authors or different papers to have a same initial quality magnitude or endpoint quality magnitude. In addition, the B-values for a given product

quality deterioration at a specific temperature would not be in agreement. However, for a specific experiment, authors have attempted to establish similar initial conditions, and maintain a standard endpoint quality. Based on this observation, the *B*-value should be constant for a product degradation of a specific experiment. From quality life data at several different temperatures, the activation energy can be obtained from plotting natural logarithm of quality life (either HQL or PSL) against the reciprocal of absolute temperature (T). The slope of this curve is equal to Ea/R.

In this investigation, the least square fitting is used to fit data of three or more available points (Table 1 thru 4) to the following equation to determine the activation energy.

$$\ln \frac{t_Q}{t_{Q,\text{ref}}} = \frac{Ea}{R}\left(\frac{1}{T} - \frac{1}{T_{\text{ref}}}\right)$$

where $t_{Q,\text{ref}}$ is the quality life at a reference temperature (T_{ref}), which is arbitrarily chosen as −18°C (255.2K) as is the generally recommended storage temperature for most frozen foods. Using this equation instead of the general form derived previously eliminated *B*-values from calculations. *B*-values are usually very small (about the order of 10^{-10}) and large variations may be introduced.

Table 1. Kinetic information of frozen foods

Product	Activation Energy kcal/mole	PSL Days (−18°C)	Reference
Beef	13.34	206	Van Arsdel (1969)
	14.81	258	Van Arsdel (1969)
roasts	12.63	368	Tressler (1957)
ground	8.68	153	Van Arsdel (1969)
Lamb	13.24	320	Tressler (1957)
Pork	26.75	316	Van Arsdel (1969)
sausage	16.12	119	Tressler (1957)
roasts	7.18	194	Tressler (1957)
Turkey	15.34	181	Van Arsdel (1969)
Chicken	20.20	282	Van Arsdel (1969)
Eggs	25.44	297	Van Arsdel (1969)
Butter	8.81	271	Van Arsdel (1969)

Table 2. Kinetic information of frozen foods

Product	Activation Energy kcal/mole	PSL Days (−18°C)	Reference
Fatty Fish	11.70	60	Van Arsdel (1969)
	10.78	185	Tressler (1957)
Lean Fish	10.17	95	Van Arsdel (1969)
	9.78	283	Tressler (1957)
cod	13.97	163	Lane (1964)
cod (canned)	10.94	193	Lane (1964)
halibut	9.76	163	Young (1950)
	9.33	420	Lane (1964)
haddock (fillet)	12.73	282	Tressler (1957)
Pollock (fillet)	15.33	181	Tressler (1957)
Smoke Fish	10.73	79	Van Arsdel (1969)
Lobster	13.10	192	Tressler (1957)
Shrimp	11.28	316	Tressler (1957)

Table 3. Kinetic information of frozen foods

Product	Activation Energy kcal/mole	PSL Days (−18°C)	Reference
Asparagus	16.15	239	Tressler (1957)
	10.51	292	Van Arsdel (1969)
Beans, snap	16.15	239	Tressler (1957)
Beans, lima	16.12	379	Tressler (1957)
Broccoli	16.12	379	Tressler (1957)
Brussel sprouts	16.15	239	Tressler (1957)
Cauliflower	16.12	379	Tressler (1957)
Corn, on cob	12.56	219	Tressler (1957)
Corn, cut	12.85	653	Tressler (1957)
Carrots	12.85	653	Tressler (1957)
Mushrooms	15.56	201	Tressler (1957)
Peas	16.12	379	Tressler (1957)
	5.88	302	Van Arsdel (1969)
Pumpkin	12.85	653	Tressler (1957)
Spinach	16.12	379	Tressler (1957)
	13.48	474	Van Arsdel (1969)
Squash	12.85	653	Tressler (1957)

Table 4. Kinetic information on frozen foods

Product	Activation Energy kcal/mole	PSL Days (−18°C)	Reference
Apricots	15.56	201	Tressler (1957)
with A.A.	16.12	420	Tressler (1957)
Peaches	15.56	201	Tressler (1957)
with A.A.	16.12	420	Tressler (1957)
Raspberry	12.72	327	Tressler (1957)
sugared	12.80	456	Tressler (1957)
Strawberry, sliced	12.80	456	Tressler (1957)

A.A.: Ascorbic acid

ANALYSIS OF FROZEN FOOD QUALITY PARAMETERS

I. Relationships of High Quality Life (HQL) and Practical Storage Life (PSL)

For a given frozen food product, HQL and PSL usually differ in their end-point magnitude (C_{tQ}) only (Van Arsdel 1969), and the same or similar reaction mode is expected. From Eq. (6), it is expected that HQL and PSL data will give the same or similar activation energy values while having different quality life values, that is, in the diagram of $\ln(t_Q)$ versus $1/T$, data of HQL and PSL will give the same or similar slopes.

Analyzing the HQL and PSL data for pork chops and calf liver (Dalhoff and Jul 1963), gives the results shown in Fig. 1. As is evident, the data does not give straight lines in the $\ln(t_Q)$ versus $1/T$ relationship, which could be due to different modes of reaction occurring at different temperature ranges or due to other reasons to be discussed later. However, the two curves (HQL and PSL) for pork chops do remain approximately parallel, i.e. similar slopes, over the temperature range of −5°C to −20°C. In the case of calf liver, two quality life lines can be represented approximately as straight lines with similar slopes in Fig. 1 for the temperature range of −5°C to −20°C.

These similarities in slope, which Jul (1968) described as "a definite relationship between the acceptability time (referred to as PSL) and the stability time (referred to as HQL)", provides an approach to reducing the time needed to carry out a commercial frozen food quality stability test; using HQL results to predict PSL of frozen foods.

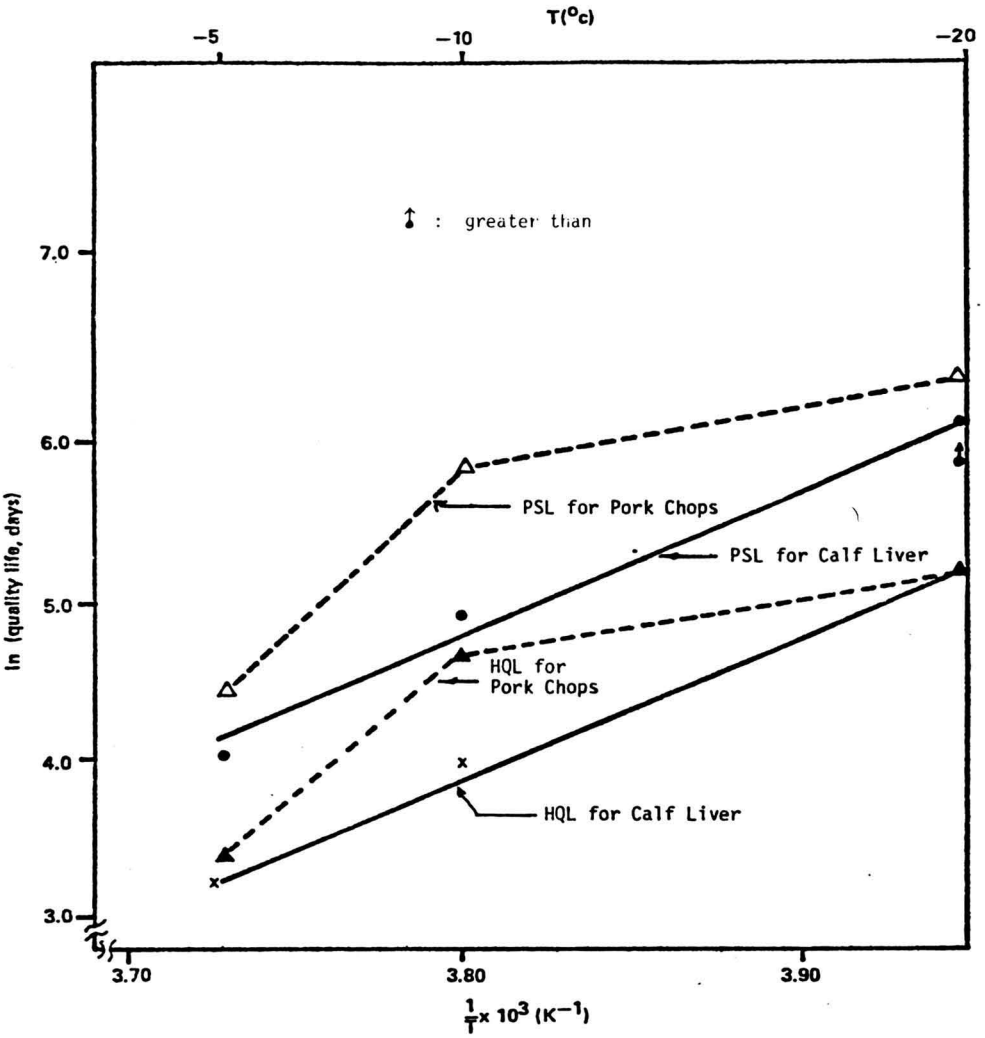

FIG. 1. RELATIONSHIPS OF HIGH QUALITY LIFE (HQL) AND PRACTICAL STORAGE LIFE (PSL) (Data from Dalhoff and Jul 1963)

II. Experimental Data

Just as overall quality magnitudes have not been quantitatively well defined, parameters such as "just noticeable change" or "acceptable quality" are equally difficult to define. Experiments performed by different authors may result in large variations in the magnitude of the parameters. It is generally considered that HQL or "just noticeable change" for frozen foods gives good reproducibility. From Eq. (6), it is

evident that initial and endpoint quality magnitudes can influence B-values and therefore t_Q (quality life) values. For a food product, it is difficult to maintain both magnitudes $[C_0]$ and $[C_{tQ}]$ constant over different experiments. Variations in the values of quality life for a given food product seem unavoidable, unless overall quality magnitudes are well defined quantitatively.

The situations are simplified only by making the initial or final quality conditions comparable for different temperature treatments in a given experiment. For a given food product, the activation energy values determined from different experiments are more comparable than the quality life values.

As can be seen from the work done by Bengtsson *et al.* (1972), which revealed that in most food products the degradation processes gave straight lines in a semilogarithmic plot of quality life versus temperature, the slopes (related to activation energy) of which could be grouped into five or six similar groups, but the variations in intercepts (related to quality life values) were too great to be predictable.

This tendency is also illustrated in Tables 1–4, although in some cases, considerable variation in activation energy values exists.

III. Variations in Activation Energies

Possible reasons for the variations in activation energy values obtained from TTT data or the deviations from the description of Eq. (6) are described as follows:

Different standards for measuring quality lives of different storage temperatures or experiments.

As deterioration of frozen foods is a composite of many contributing reactions, the end of a given quality life may be detected from oxidative deterioration, e.g. ascorbic acid oxidation, color change, lipid oxidation, protein denaturation, or a combination of several quality characteristics. There is no doubt that quality life data established by following the changes of a specific quality component or characteristic may result in different quality life values if the components being detected are different, as in the case of flavor changes and color changes for beans (Dietrich *et al.* 1959).

For the detection of quality life by measuring the overall quality or a combination of several contributing factors, the relative importance of these contributing factors may vary as storage temperature differs. This variation in relative importance will result in different quality life values and activation energy values. As in the following case, by analyzing quality life data of color and flavor changes of spinach, the relation between quality life and temperature can be shown as in Fig.

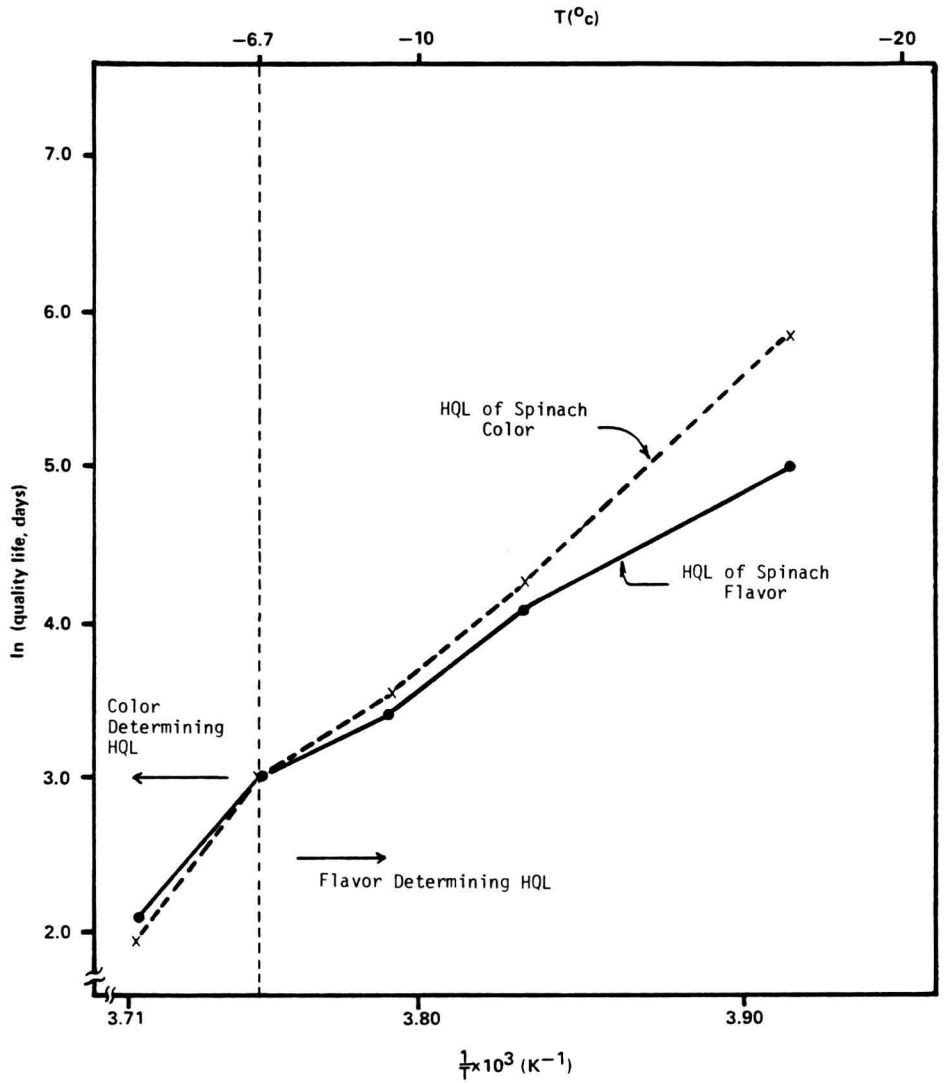

FIG. 2. OVERALL HQL OF SPINACH AS A COMPOSITE OF COMPONENT HQL'S (Data from Dietrich *et al.* 1962)

2. Assuming the overall quality change is described by a composite contribution of color and flavor changes, then for storage temperature lower than about −6.7°C, the major contribution to establishing the end of quality life would be Flavor change, while for temperature higher than this, the major contributing factor would be color change. Different experiments or even different storage temperature treat-

ments for an experiment may account for different proportions of contributing factors when measuring the end of a quality life; and result in variations in activation energies.

Considering a limiting case, where overall quality is influenced by many factors, then as shown in Fig. 3, the relationship between ln t_Q versus $1/T$ will be a concave downward curve and in some cases, t_Q, instead of ln t_Q, versus $1/T$ will give a linear relationship. HQL data of pork chops (Van Arsdel 1969) illustrated the expected concave downward-shaped curve over the temperature range of −9°C to −24°C when plotting ln t_Q versus $1/T$, and a linear relationship when plotting t_Q versus $1/T$ (Fig. 4). This indicates that over lower temperature ranges, temperature change will have less influence on the rate of change (or quality life value) than over higher temperature ranges. For the temperature range of −24°C to −40°C, however, there exists a section of abrupt increase in the slope and activation energy. This could be due

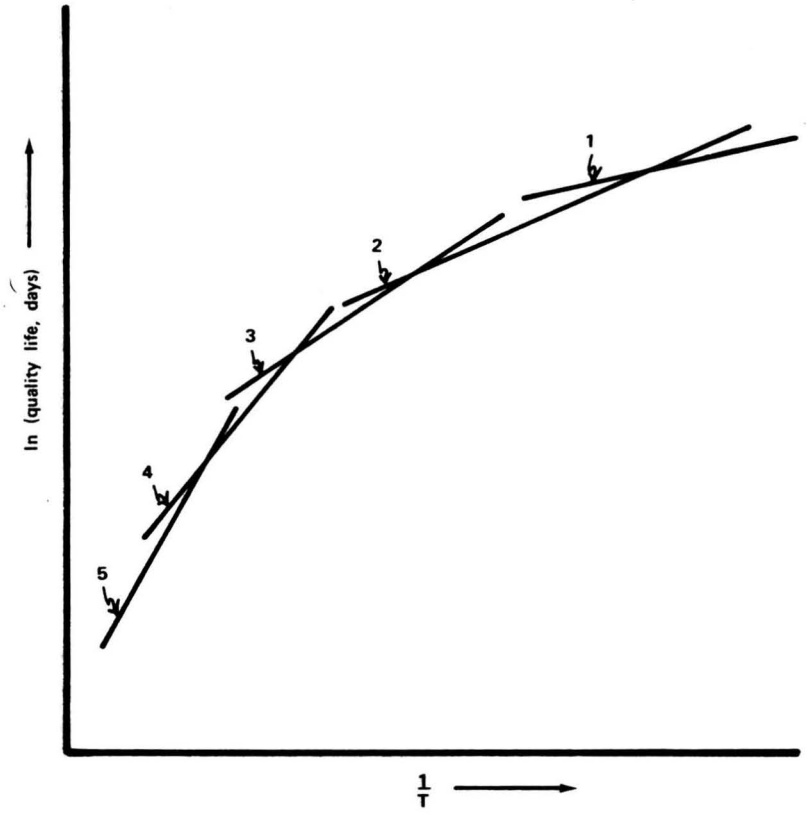

FIG. 3. QUALITY LIFE DETERMINED BY A COMBINATION OF FIVE CONTRIBUTION FACTORS

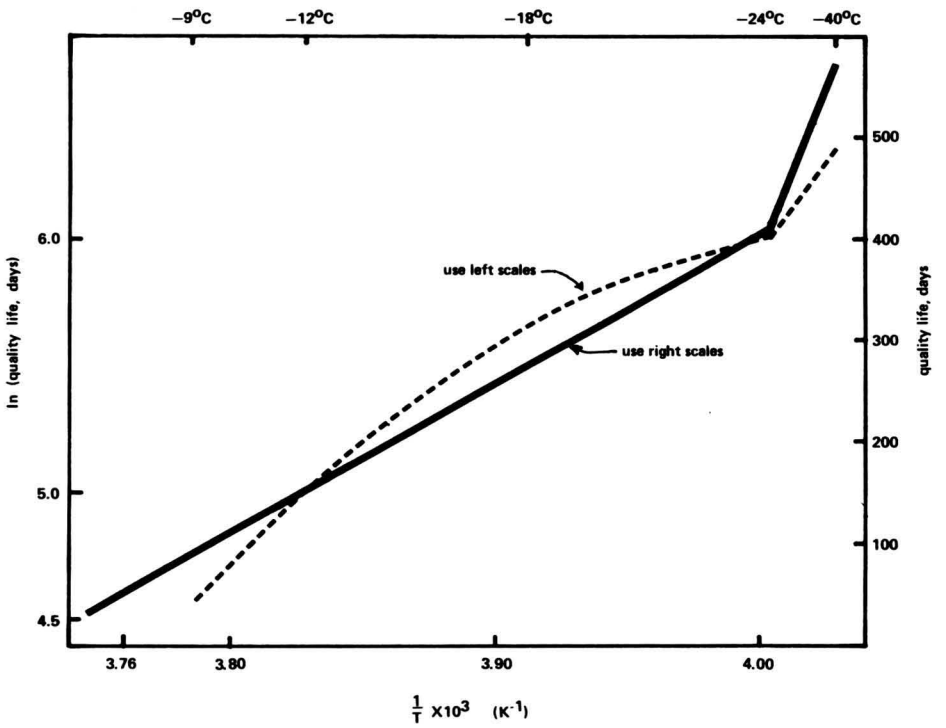

FIG. 4. HQL FOR PORK CHOPS AS IN $\ln t_Q$ VERSUS $\frac{1}{T}$ AND t_Q VERSUS $\frac{1}{T}$ (Data adapted by Van Arsdel 1969, from Bøgh-Sørensen)

to the fact that at this low temperature range, changes of all previously described contributing factors have ceased and a "low temperature contributing factor" begins to contribute, with a characteristic of high activation energy. Based on this analysis, some contributing factors may cease at certain temperature ranges and it is evident that in principle all possible forms of curve shape can occur when plotting $\ln t_Q$ versus $1/T$. In practical situations, however, the temperature ranges are small and only several contributing factors are involved. Tracing the change in each contributing factor and combining into the $\ln t_Q$ versus $1/T$ plot may give a good description of the overall quality changes.

An alternative explanation for this abrupt increase in slope is accounted for by the "negative temperature effect" described as follows.

Negative Effect of temperature.

For certain reactions, the concentration effect may counteract the temperature effect on the reaction rate and therefore disturb the

regular picture of the Arrhenius relationship. Pincock and Kiovsky (1966) used a dilute binary system to reveal this phenomenon. Freeze concentration is only one of the several possible reasons for the negative effect of temperature as described by Fennema (1973).

Works done by Brown and Doler (1963) on oxidation of myoglobin solution from beef and tuna, Anderson and Ravesi (1969) on reaction of free fatty acid with protein in cod muscle, Behnke *et al.* (1973) on glycolysis of chicken and beef, Lindelov and Poulsen (1978) on smoked bacon, liver paste and chopped herring fillets and Poulsen *et al.* (1976) on butter all reported this negative temperature effect. Singh and Wang (1977) give a thorough review on research reporting negative temperature effect.

Variations in initial or final quality magnitudes for a given experiment.

From Eq. (6), it can be seen that variations in $[C_0]$, $[C_{tQ}]$ values will give variations in t_Q values. These variations in t_Q values usually give a nonstraight line relationship between $\ln t_Q$ and $1/T$ and make the determination of correct activation energy difficult or impossible.

HQL data of cut-up stewing hens at four different temperatures (Klose *et al.* 1959) are presented in Fig. 5. These HQL values can be divided into two groups. The first group, HQL's at −6.7°C and −12.2°C, were obtained by detecting just noticeable difference against a controlled sample stored at −23.3°C. The second group, HQL's at −17.8°C and −23.3°C, was detected against the controlled sample stored at −34.4°C. From the classification, it can be seen that the assumed initial quality magnitude for two groups, one as the controlled sample at −23.3°C storage and the other at −34.4°C storage, were different.

This difference in initial quality magnitudes gives a difference in B values for the two groups, while the reaction mode or activation energy remains unaffected. These two groups of data result in two parallel straight lines on the plot of $\ln t_Q$ versus $1/T$. Determination of activation energy in this case should be based on each group separately, instead of considering all four data points.

Variations in packaging material and other factors influencing the quality concentration or reaction mode.

Effect of packaging or other factors on the magnitudes of activation energies depends on the characteristics of the factors. If these factors influence quality magnitude only, then activation energies obtained under the influence of these factors still give the same activation energy values, as long as data obtained under different conditions are treated separately. If the factors influence the reaction modes, then both quality lives and activation energies are not comparable when the data are obtained under different treatment magnitudes.

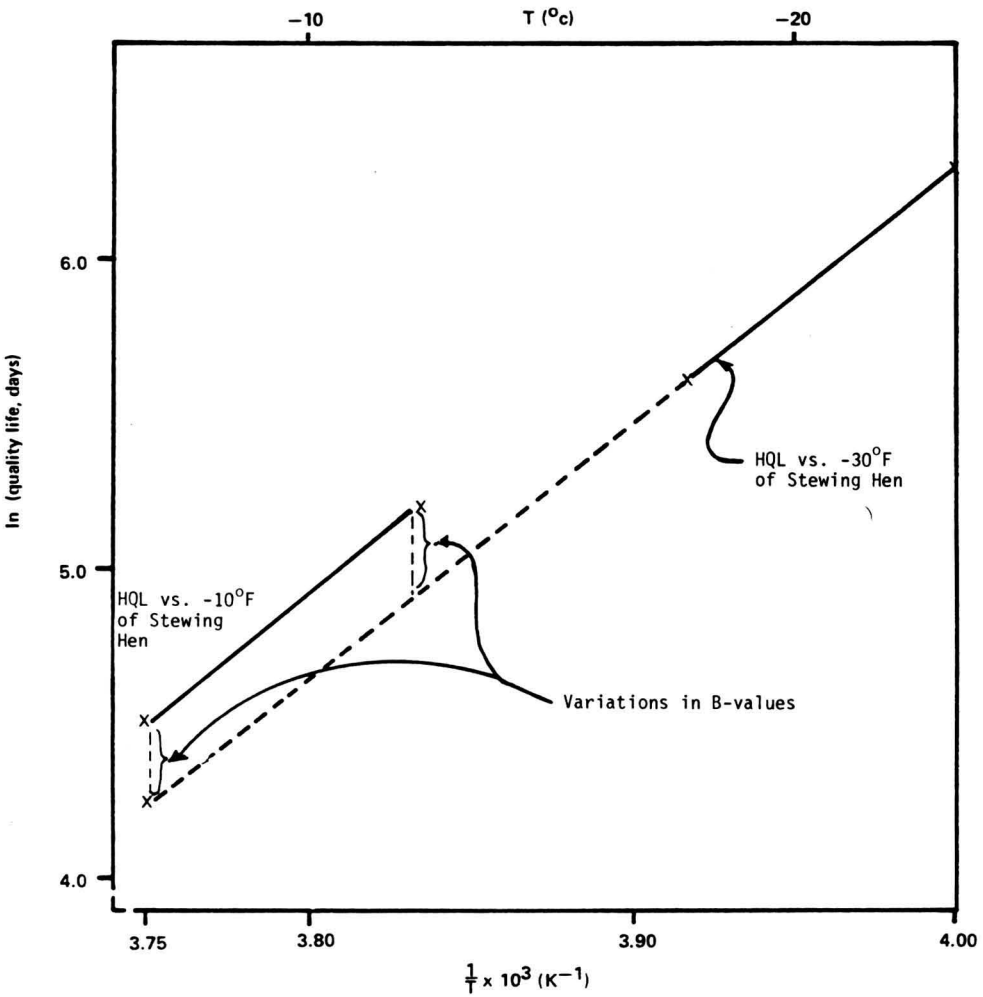

FIG. 5. VARIATIONS IN ACTIVATION ENERGIES DUE TO VARIATIONS IN *B*-VALUES EXEMPLIFIED BY HQL OF RAW MEAT ODOR OF STEWING HEN (Data from Klose *et al.* 1959)

HQL data for cut-up chicken (Klose *et al.* 1959) in Fig. 6 illustrate the influence of packaging on quality life and activation energy. For the plot of $\ln t_Q$ versus $1/T$, good packaging and poor packaging give similar slopes and activation energies. For the product exposed to atmosphere, the reaction mode at higher temperature range seems to be different from the two conditions discussed previously. The quality life values are largest for good packaging conditions and smallest for product exposed to atmosphere.

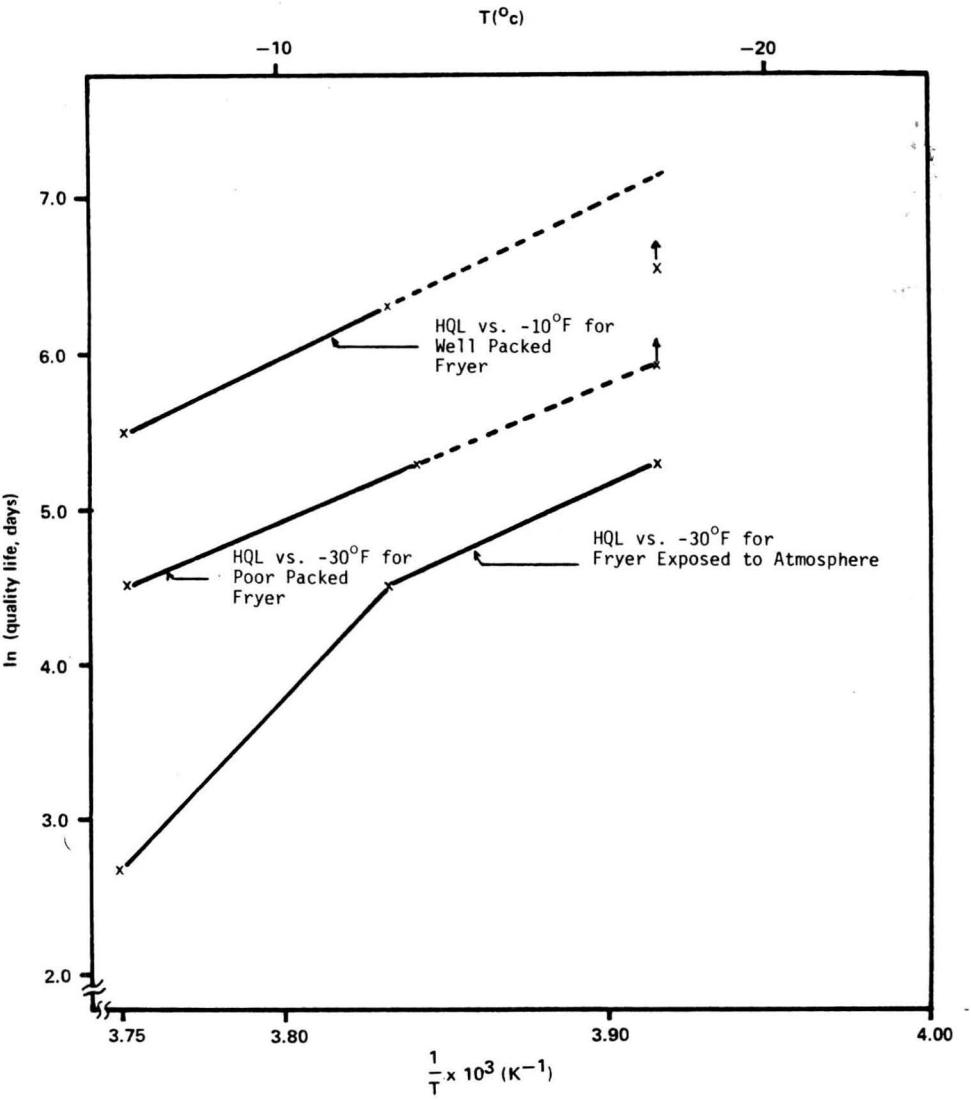

FIG. 6. EFFECT OF PACKAGING ON HQL OF CUT-UP CHICKEN PRODUCTS (Data from Klose *et al.* 1959)

PROPOSED PROCEDURES FOR KINETIC ANALYSIS

When applying the following procedures, it should be realized that the model describes the specific quality parameters and units which are used in evaluating kinetic parameters, e.g., if an *Ea* value is determined from color rating, then the resulting prediction can be used to describe

the color rating only; while for an *Ea* value determined from chrophyll conversion, the prediction then can be used to describe chrophyll conversion only. The magnitude of quality parameter $[C]$ can be of any kind quality rating, as long as the above principle is kept when applying the prediction model.

I. Analysis based on zero order assumption

$$k_0 = \frac{1-\alpha}{t_Q}$$

$$dX = k_0\,dt$$

From Arrhenius Equation

$$k_0 = A\,\exp\left(\frac{-Ea}{RT}\right)$$

$$k_{0,T} = k_{0,T_1}\cdot\exp\left[\frac{-Ea}{R}\left(\frac{1}{T}-\frac{1}{T_1}\right)\right]$$

let $T_1 = 255K$

$$k_{0,255} = \frac{1-\alpha}{t_{Q,255}}$$

from

$$[C_0]-[C_t] = \Delta X = \int_{t_0}^{t} k_0\,dt$$

$$[C_t] = [C_0] - \int_{t_0}^{t}\frac{(1-\alpha)[C_0]}{t_{Q,255}}\cdot\exp\left[\frac{-Ea}{R}\left(\frac{1}{T(t)}-\frac{1}{255}\right)\right]dt$$

usually, $[C_0]$, $[C_t]$ can not be expressed in absolute quantities. Dividing both sides by $[C_0]$, then $[C_t]$, can be expressed in terms of fraction of $[C_0]$ as:

$$\frac{[C_t]}{[C_0]} = 1 - \int_{t_0}^{t}\frac{(1-\alpha)}{t_{Q,255}}\cdot\exp\left[\frac{-Ea}{R}\left(\frac{1}{T(t)}-\frac{1}{255}\right)\right]dt$$

By knowing temperature history, i.e., temperature as a function of time, T(t), the integrals can be integrated to obtain suitable expression to describe or predict quality change.

II. Analysis based on first order assumption

$$k_1 = \frac{-\ln \alpha}{t_Q} \qquad \frac{dX}{[C_0 - X]} = k_1 dt$$

From Arrhenius equation

$$k_{1,T} = k_{1,T_1} \cdot \exp\left[\frac{-Ea}{R}\left(\frac{1}{T} - \frac{1}{T_1}\right)\right]$$

let $T_1 = 255K$

$$k_{1,255} = \frac{-\ln \alpha}{t_{Q,255}} \qquad \ln \frac{[C_t]}{[C_0]} = -\int_{t_0}^{t} k_1 dt$$

$$[C_t] = [C_0] \cdot \exp\left\{\int_{t_0}^{t} \frac{\ln \alpha}{t_{Q,255}} \cdot \exp\left[\frac{-Ea}{R}\left(\frac{1}{T(t)} - \frac{1}{255}\right)\right]\right\} dt$$

To express $[C_t]$ as a fraction of $[C_0]$,

$$\frac{[C_t]}{[C_0]} = \exp\left\{\int_{t_0}^{t} \frac{\ln \alpha}{t_{Q,255}} \cdot \exp\left[\frac{-Ea}{R}\left(\frac{1}{T(t)} - \frac{1}{255}\right)\right]\right\} dt$$

Again, by knowing temperature history, $T(t)$, the integrals can be determined to describe quality change.

CONCLUSIONS

Time-Temperature-Tolerance (TTT) data can be treated to obtain activation energies for the overall quality change of frozen foods based on the following equation,

$$\ln t_Q = \ln B + \frac{Ea}{R}\frac{1}{T}$$

Reaction order and reaction rate constant are difficult to obtain from TTT experiments. As an approximation, a suitable reacton order can be assumed to get an expression for the reaction rate constant. This expression can be incorporated into the Arrhenius equation to describe overall quality magnitude in terms of fraction of initial quality magnitude. The expression based on the first order reaction assumption is:

$$\frac{[C_t]}{[C_0]} = \exp\left\{\int_{t_0}^{t} \frac{\ln \alpha}{t_{Q,255}} \cdot \exp\left[\frac{-Ea}{R}\left(\frac{1}{T(t)} - \frac{1}{255}\right)\right]\right\} dt$$

while the expression based on zero order reaction assumption is

$$\frac{[C_t]}{[C_0]} = 1 - \int_{t_0}^{t} \frac{1-\alpha}{t_{Q,255}} \cdot \exp\left[\frac{-Ea}{R}\left(\frac{1}{T(t)} - \frac{1}{255}\right)\right] dt$$

The major difficulty associated with the kinetic analysis of frozen food quality degradation is that a quantitative definition of overall quality magnitude has not been established. To deal with this situation, the changes of each of the major quality factors should be traced and combined with the kinetic information to describe overall quality change. In this case, a curved line on the plot of $\ln(t_Q)$ versus $1/T$ relationship may be used.

For the purpose of kinetic analysis, quality life (HQL or PSL) can be useful only when the initial and endpoint quality magnitude are comparable, which may come into concern when dealing with different temperature treatments for the determination of activation energy, or dealing with different experiments for the adaptability of quality life.

NOTATIONS

A	pre-exponential of Arrhenius equation ratio of $[C_{tQ}]/[C_0]$
B	pre-exponential in the equation between t_Q and $1/T$, a function of $[C_0]$, $[C_{tQ}]$, and A
C,D	quality of parameters related to reaction rate
Ea	activation energy
k	reaction rate constant
R	universal gas constant
T	absolute temperature
t	time variable
t_Q	quality life, HQL or PSL
X	quality magnitude variable
[]	magnitude of quality parameter

Subscripts

tQ	at the end of quality life
0	initial condition

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PREDICTING AVAILABLE LYSINE LOSSES DURING HEAT PROCESSING[1]

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ABSTRACT

Mathematical models, which are amalgams of empirical equations and reaction kinetics, were used to predict the destruction of available lysine in proteins. R^2-values for plots of predicted versus observed values ranged from 0.8 to 0.9. Changes in water activity, sugar, salt, oil, pH, time and temperature are considered by the model. The model can adjust for different sugars by employing an algorithm based upon the mutarotation constant for a specific sugar. A plot of sugar mutarotation constant against the appropriate loss rate coefficient demonstrated the relation between these two measures ($R^2 = 0.8$). Nomograms for predicting the loss rate coefficient and the activation energy, which can be used in an industrial application, are presented.

INTRODUCTION

Lysine, the limiting amino acid in cereal grains, is often destroyed during food processing and storage. Although several chemical loss mechanisms including thermalysis, protein-protein interactions and protein-amino acid interactions (Bjarnason and Carpenter 1970) account for some loss, Maillard browning is the major factor responsible for lysine losses. Food manufacturers attempt to minimize lysine losses

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due to Maillard browning by employing techniques which have evolved from research on brown color formation. These measures include control of product moisture, pH, sugar type (Hodge and Osman 1976) and sulfite levels (Burton *et al.* 1962).

Thompson, in a series of studies on essential amino acid loss during processing (Jokinen *et al.* 1976; Thompson *et al.* 1976; Wolf *et al.* 1977, 1978, 1981; Thompson and Wolf 1979), examined the influence of product composition, process variables and cooking methods on protein lysine, free lysine and free methionine losses due to Maillard browning. The concluded that: (1) the loss of these amino acids could be predicted as a function of the previously mentioned variables and (2) that mathematical models which combine reaction kinetics and empirical functions could be used to minimize amino acid loss during processing.

The overall objective of this study was to expand the mathematical lysine loss prediction models presented by Wolf *et al.* (1977). A more comprehensive model was constructed which considers in addition to the previously studied effects of sugar level, pH, water activity, time and temperature, the effects of sugar type, salt and oil level. The usefulness of the model was also expanded by developing a simplified graphical version (Kline 1968) of the mathematical equations.

MATERIALS AND METHODS

Sample Preparation

Although a variety of food system compositions and process conditions were employed in this study, the sample preparation procedures were similar. The ingredients, except for fatty acids or the oil-prooxidant mixture, were first dry blended and then slurried with either a minimal volume (1.5:1, V/W) of a pH 7.0 phosphate buffer (0.1M) or distilled water to evenly distribute the soluble components of the system. Any required pH adjustments were then accomplished by adding either 1.0M HCl or 1.0M NaOH solutions to the slurry. The slurried samples were placed into shallow pans, quick frozen in a −80 C freezer or a −30 C blast freezer and then freeze dried. The dried samples were ground to a powder and the designated quantity of fatty acid or oil-proxidant mixture incorporated into the sample. The samples were then equilibrated to the desired water activity (a_w) under a partial vacuum in desiccators containing saturated salt solutions. After achieving the desired a_w, the samples were sealed in retortable foil pouches (50M-35F-300097-R2 retort stock, Continental Can Company).

The samples were processed using near isothermal conditions (60-125 C) without stirring. Sample processing was performed in water baths when temperatures were less than 100 C. Above 100 C, sample processing was performed in miniature retorts (Schmidt *et al.* 1955). Heating and cooling lags which occurred during retort processing were offset by employing an adjustment method similar to the one proposed by Gondo *et al.* (1972). After processing, the samples were immediately cooled by immersion into an ice-water bath. Process times were chosen to give from 0 to 90% reactive lysine destruction.

Sugar Experiments

1. Nonlinear glucose effect. Model food systems composed of 15% soy protein isolate (Promine D, Central Soya), the design level of glucose and microcrystalline cellulose (Avicel, FMC Corp.) to 100% (Table 1) were prepared as described in the previous section. Sample pH was adjusted to 7.0 while the initial water activity was 0.68. The samples were processed at 105 C for 13 min.
2. Sugar type. Model food systems composed of 15% soy protein isolate, sugar (0.00333M), salt (NaCl) and microcrystalline cellulose to 100% (Table 2) were prepared. Sugar, salt level and water activity were set according to design specifications. Two process temperatures (80 and 125 C) were used with the process time chosen to obtain from 10 to 50% destruction.

Model Development Experiment

Model food systems were prepared. The sample pH, water activity, glucose, salt (NaCl) and oil (stripped corn oil, Kodak) levels were varied according to design specifications (Table 3). The protein level (15%) was held constant and microocrystalline cellulose was used to bring all samples to 100%. The samples were processed at 80 and 125 C for 555 min and 1.5 min, respectively.

Table 1. Influence of glucose level on reactive lysine loss rate[a]

% glucose	0.1	1.1	1.5	2.1	2.8	3.1	4.1	6.1
Absolute loss rate (mg/g sample · min)[b]	0.3	1.2	1.4	2.1	2.8	4.2	5.2	8.4

[a] samples were processed at 105 C for 13 min.
[b] mean of five replications

Table 2. Influence of sugar type on the lysine loss rate coefficent

Sugar	Amount (%)	NaCl (%)	a_w	Temp (C)	Time (min)	k_T (1/min) Mean	Std. Dev.
Xylose	3.34	—	.68	125.	2.25	2.610	0.350
Glucose	4.00	0.0	.68	125.	2.25	1.580	0.300
Glucose	4.00	0.0	.68	80.	420.0	0.015	0.002
Glucose	4.00	3.0	.68	125.	2.25	1.388	0.151
Glucose	4.00	3.0	.68	80.	420.0	0.010	0.001
Glucose	4.00	0.0	.23	125.	2.25	2.083	0.001
Glucose	4.00	0.0	.23	80.	420.0	0.015	0.001
Fructose	4.00	—	.68	125.	12.0	0.082	0.001
Lactose	8.00	0.0	.23	125.	15.0	0.489	0.008
Lactose	8.00	0.0	.23	80.	1400.0	0.006	0.000
Lactose	8.00	0.0	.68	125.	15.0	0.400	0.065
Lactose	8.00	0.0	.68	80.	1400.0	0.005	0.000
Lactose	8.00	3.0	.68	125.	15.0	0.430	0.105
Lactose	8.00	3.0	.68	80.	1440.0	0.050	0.000
Maltose	8.00	—	.68	125.	15.0	0.229	0.006
Sucrose	7.60	—	.68	125.	15.0	0.017	0.001
Raffinose	13.20	—	.68	125.	20.0	0.027	0.003

Table 3. Code and actual treatment levels for prediction model construction

Variables	−2.38	−1.00	Code Level 0.00	+1.00	+2.38
			Actual Level		
Sugar (%)	0.24	3.00	5.00	7.00	9.76
Salt (%)	1.62	3.00	4.00	5.00	6.38
pH	4.62	6.00	7.00	8.00	9.38
Oil (%)	0.48	6.00	10.00	14.00	19.52
a_w	0.22	0.44	0.60	0.76	0.98
Process temp. (C)		80	125		
Process time (min)		555	1.50		

Chemical Analysis

Samples were analyzed for reactive lysine and moisture. Reactive lysine was measured by the fluorodinitrobenzene method (FDNB) of Carpenter (1960) as modified by Peterson and Warthesen (1979). Sample moisture content was determined by utilizing the gas-chromatographic procedure of Hollis and Hayes (1966) as modified by Reineccius and Addis (1973). Extraction time was increased to four hours to insure a complete extraction.

Experimental Design

Zero time controls were run in all experiments to obtain values for the reaction coefficients and to provide a check for shifting lysine values due to time of analysis. Unless specified, three replications of each treatment were employed. The processed samples were randomized prior to analysis.

Nonlinear Glucose Effect. The mathematical models (Wolf *et al.* 1977) suggest that there may be two independent reaction mechanisms involving glucose and lysine. This experiment examined the possibility by utilizing glucose levels which were located at critical portions of the model generated loss rate curve. Sensitivity coefficients were used to determine glucose levels (Table 1). A randomized design with a full factorial allocation using five replications per treatment was employed. Samples were analyzed according to a randomized block design in which one complete concentration series was a block.

Sugar Type Effect. Research by Lewis and Lea (1950) and Spark (1969) suggests that models which do not consider both sugar-level and type would fail if a sugar other than that used in the model development was tested. This experiment examined how sensitive lysine loss rate coefficients were to sugar type at elevated temperatures, the degree to which model coefficient values were altered and if there was a mathematical relationship between sugar mutarotation constants and lysine loss rate coefficients.

A randomized design using a fractional factorial allocation was employed. The allocation allowed sugar main effects to be noted. Sugar-sugar interactions were not studied. Salt and water-activity were varied for two sugars, glucose and lactose (Table 2), according to a fractional factorial allocation. The low water activity and high salt combination was omitted. Any significant changes in model salt and water activity coefficient terms could be noted by t-testing the coefficient values of equations one and two.

$$k_g = a_i + b_i X_1 + c_i X_2 \tag{1}$$

$$k_l = a_i + b_i X_1 + c_i X_2 \tag{2}$$

where k_g = lysine loss rate coefficient (glucose) at 100 C
k_l = lysine loss rate coefficient (lactose) at 100 C
a_i = constant plus sugar main effect coefficient
b_i = water activity term coefficient
c_i = salt term coefficient
X_1 = coded water activity level
X_2 = coded salt level

While all samples were processed at 125 C, glucose and lactose containing samples were also processed at 80 C. Therefore the reference loss rate coefficient (k_{100}) and activation energy (E_a) for samples containing glucose and lactose were calculated and used for variable coefficient tests.

The relationship between sugar mutarotation constants and lysine loss rate coefficients was examined by utilizing linear least square analysis. The R^2-value was employed to provide a measure of fit.

Construction of Prediction Models. The mathematical models predict k_{100} and E_a as a function of product composition. The k_{100} and E_a values are then used in an Arrhenius equation to predict k_T at the desired temperature. The k_T value is then used in a first order reaction equation which gives the amount of available lysine destruction for any process period.

A rotatable central composite design (Cochran and Cox 1957) was employed to assign variables (Table 3). In the absence of fatty acids or oil, the soy isolate utilized in the study as a no-loss phase (Thompson *et al.* 1976) which commences at 55% lysine loss. Since several treatments contained only minimal amounts of oil and therefore could conceivably have a no loss phase, the process times were selected to obtain from 0 to 50% destruction. The E_a and k_{100} values estimated for each treatment combination were subjected to multiple regression analysis using SPSS (Nie *et al.* 1975) and Multreg (Weisberg 1979). The adjusted R^2 value and C_p-statistics were used to choose the best equations.

Model Verification. Data from previous experiments (1976-1979) were compared with model predictions. Actual measured fraction remaining lysine values were plotted against model predicted values using linear least square analysis. The best fit line was analyzed using slope, intercept and R^2-values as a measure of model success.

RESULTS AND DISCUSSION

Nonlinear Glucose Effect. Lysine loss at elevated temperatures in the presence of sugar due to Maillard browning is reported as first order in lysine (Thompson *et al.* 1976). However, a mathematical model (Wolf *et al.* 1977) suggests that there are two independent loss mechanisms involving lysine and glucose. The lysine loss rate versus glucose concentration plot generated by that model's predictions show a three step process. The first step is a linear increase phase followed by a saturation phase which occurs at the glucose-lysine saturation

ratio noted by Hannan and Lea (1952). This second phase is then followed by another linear increase phase in the loss rate.

The absolute lysine loss rate versus glucose concentration study (Table 1) using glucose concentration set by sensitivity coefficient shows only a linear relationship even when glucose levels as high as 6.1% were employed. A 6.1% sugar level and 15% protein level result in a molar ratio greater than 3:1. This causes a saturation effect as noted by Hannan and Lea (1952). Force fit regression models generated from the data which use glucose linear and cube functions demonstrate that there is only a linear increase in the absolute loss rate with increasing sugar over the sugar concentrations used (Eq. 3 and 4).

Generated Equations	F-value	R^2-value	F-value for Lack of Fit	
Lysine (mg/g sample · min) = (0.025 + 0.028 * Glucose)	121	0.75	0.23	(3)
Lysine (mg/g sample · min) = (0.027 + 0.012 * Glucose)	55	0.56	4.47	(4)

Influence of Sugar Type. The research of Lewis and Lea (1950) and Spark (1969) concerning relative lysine loss or browning with various sugars suggests the need for a term which would modify the sugar variable term in the mathematical models. In reactions with amino acids at room temperature where brown color formation was monitored, Spark (1969) noted that aldopentoses reacted fastest, followed by aldohexoses, ketohexoses, disaccharides and trisaccharides. The need for the prediction model to consider sugar type, in addition to sugar level, is clearly shown when various sugar types react with protein lysine at elevated temperatures (Table 2). Mathematical models developed with one sugar to preduct lysine loss will incorrectly predict that loss if a different sugar type is present, unless the difference in reactivity is considered by the model.

Ellis (1959) and Overend *et al.* (1961) noted that sugar reactivity is associated with the conformational stability of the sugar. Therefore several weighting methods, such as percent of open chain sugar, sugar equilibrium constant or sugar mutarotation constant, might form the basis for an algorithm which would be used by the model to alter the influence of the sugar term. Since the sugar concentrations (mole basis) were equal in this experiment, it appears that a measure of sugar conformational stability might form the basis for the algorithm.

Therefore, mutarotation values at 20 C for various sugars (Pigman and Isbell 1968) were examined to determine if there was a simple relationship between the lysine loss rate coefficient and the appropriate sugar mutarotation constant. A best fit line (Fig. 1) demonstrated a linear relationship between the sugar mutarotation constant and the associated lysine loss rate coefficient. Therefore a straight line equation which equates the mutarotation constant to the lysine loss rate coefficient can be used to generate the sugar coefficient term and the equation constant.

The influence of sugar types on other variable coefficient values has not been completely defined. However, preliminary analysis suggests that sugar type may also influence model coefficients for terms not involving sugar. For example, significant differences ($\alpha < 0.05$) occurred in both water activity and salt terms for the rate coefficient and activation energy equations when the sugar source was changed from glucose to lactose (Table 4). Further experimentation is required before the nature of the appropriate weighting factor can be defined.

Construction and Testing of Mathematical Model. The mathematical model consists of four parts: (1) two empirical equations to predict reference rate coefficients at 100 C (k_{100}) and the apparent activation

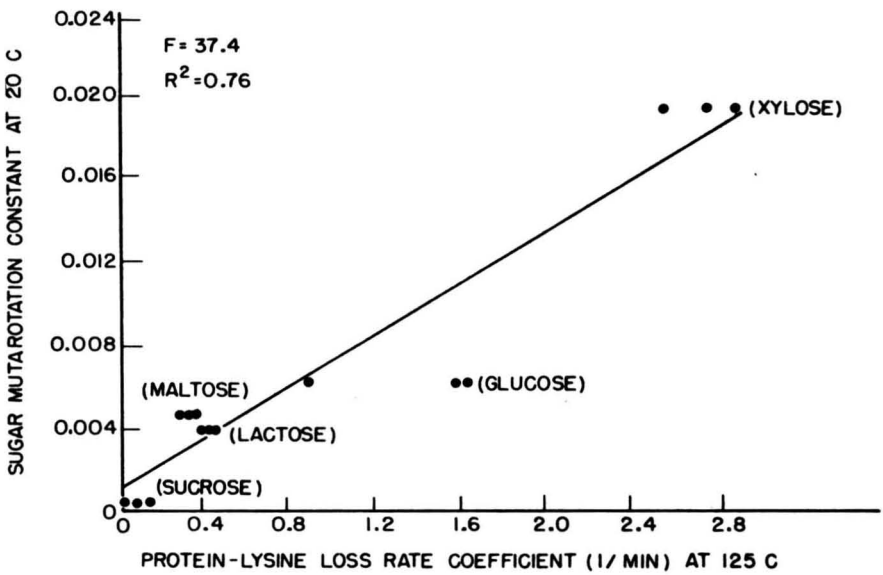

FIG. 1. REGRESSION BETWEEN MUTAROTATION CONSTANTS FOR TESTED SUGARS AND PROTEIN LYSINE LOSS RATES FOR ASSOCIATED SUGARS

Table 4. Influence of sugar type on equation coefficient values

Sugar	a_w	Salt (%)	$k_{100}(\text{min}^{-1})$ Mean	E_a(kJ/mole) Mean
Glucose	0.68	0.0	0.014	119.7
Glucose	0.68	3.0	0.010	128.9
Glucose	0.23	0.0	0.015	128.9
Lactose	0.23	0.0	0.050	113.0
Lactose	0.68	0.0	0.040	112.6
Lactose	0.80	3.0	0.043	113.4

$k_{100}(\text{Glucose}) = 0.015 - 0.0018 * a_w - 0.0034 * \text{salt (1/min)}$
$k_{100}(\text{Lactose}) = 0.005 - 0.0010 * a_w + 0.0003 * \text{salt (1/min)}$
T-value 28.6[a] 0.60 6.15[a]
$E_a(\text{Glucose}) = 128.9 - 2.2 * a_w + 2.3 * \text{salt (kJ/mole)}$
$E_a(\text{Lactose}) = 113.0 - 0.1 * a_w + 0.2 * \text{salt (kJ/mole)}$
T-value 8.88[a] 1.12 2.8[a]
a = Significant at $\alpha \leq 0.05$

energy (E_a) as a function of food composition, (2) the Arrhenius equation (Eq. 5) to calculate k_T where:

$$k_T = k_{100} \exp[-E_a(1/T_a - 1/373.15)/R] \quad (5)$$

R = gas constant (8.314 J/g-mole K)
T_a = absolute temperature (K)
E_a = apparent activation energy (J/g-mole)
k_T = loss rate coefficient at temperature T (min^{-1})
k_{100} = reference rate coefficient at 100 C (min^{-1})

and (3) the first order rate equation (Eq. 6 and 7) which predict the fraction of protein lysine remaining where

$$dC/dt = -k_T C \text{ with } C = C_0 \text{ at } t = 0 \quad (6)$$

C = lysine remaining at a specific time (mg/g sample)
C_0 = lysine level at zero time (mg/g sample)
t = process time (minutes)
k_T = rate coefficient at temperature T (min^{-1})

If the process is isothermal, the equation integrates to:

$$C/C_0 = \exp -(k_T t) \quad (7)$$

Linear, polynomial, power and exponential equations for predicting k_{100} and E_a as a function of product composition were constructed using the computer routines described previously. In general either polynomial (Eq. 8) or exponential relationships (Eq. 9) of the following forms best explained the variation during the regression analysis.

$$E(y) = B_0 + \sum_{i=1}^{k} B_i x_i + \sum_{i \leq j}^{k} B_{ij} x_i x_j \quad (8)$$

$$E(\log(y)) = B_0 + \sum_{i=1}^{k} B_1 x_1 + \sum_{i \leq j}^{k} B_{ij} x_i x_j \quad (9)$$

$E(y)$ = predicted response level
k = the number of independent variables in the experiment
x_i, x_j = the level of independent variable i or j
B_0 = constant
B_i, B_{ij} = coefficient in the model
Σ = summation

The best equations (C_p criterion or R^2-value) from the hundreds of generated equations were selected for testing (Table 5).

Several combinations of k_{100} and E_a equations when used in conjunction with the Arrhenius equation (5) and the first order rate equation (6) accurately predicted lysine loss in the verification experiment (Fig. 2). The R^2-value, slope and intercept values were employed to determine model accuracy (Table 6). As described previously, model response

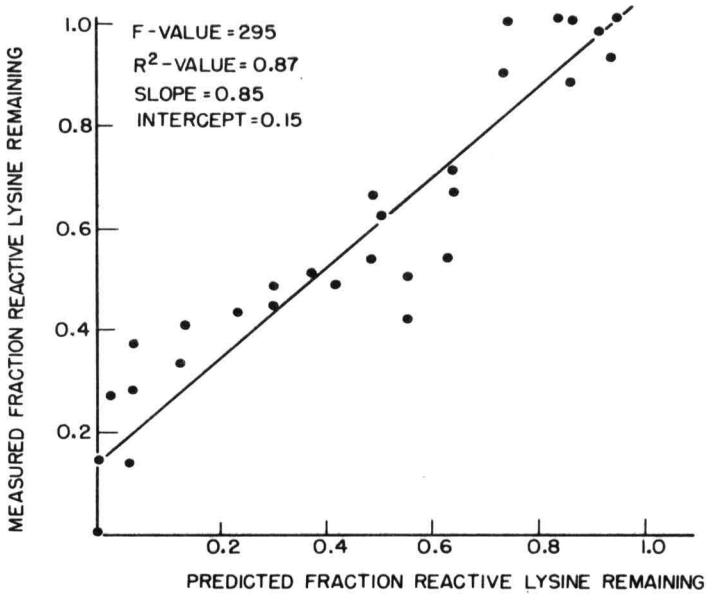

FIG. 2. REGRESSION BETWEEN MATHEMATICAL PREDICTED PROTEIN LYSINE LOSS AND MEASURED LOSSES Equations 4 and 7 from Table 6 were used to predict fraction lysine remaining in the test plot.

Table 5. Equations to predict reference rate coefficient (k_{100} min^{-1}) and activation energy (kJ/mole)

Equation

1. $\text{Log}(k_{100}) = -1.51 + 0.22 * G - 0.21 * a_w - 0.11 * G^2 - 0.09 * a_w^2 - 0.06 * \text{pH} * \text{oil}$
2. $\text{Log}(k_{100}) = -1.47 + 0.11 * G - 0.20 * a_w - 0.28 * G^2 - 0.09 * a_w^2 - 0.06 * \text{pH} * \text{oil} + 0.06 * G * a_w - 0.16/(G + 2.5) - 0.03/(S + 2.5)$
3. $\text{Log}(k_{100}) = -1.54 + 0.28 * G - 0.26 * a_w - 0.15 * G^2 - 0.11 * a_w^2 + 0.1 * G * \text{oil}$
4. $\text{Log}(k_{100}) = -1.51 + 0.09 * G - 0.20 * a_w - 0.06 * \text{pH} * \text{oil} + 0.06 * G * a_w - 0.16/(G + 2.5) - 0.08 * a_w^2$
5. $\text{Log}(k_{100}) = -1.49 + 0.09 * G - 0.17 * a_w - 0.19 * a_w^2 - 0.06 * \text{pH} * \text{oil} + 0.06 * G * a_w - 0.16/(G + 2.5) - 0.02/(\text{pH} + 2.5) + 0.04/(a_w + 2.5)$
6. $k_{100} = 0.03 - .001 * a_w^2 + 0.01 * (G + S) + 0.01 * (G + \text{oil}) - 0.01 * (G + a_w) - 0.01 * (S + \text{oil})$
7. $E_a = 138.08 + 0.99 * G - 1.78 * a_w + 1.82 * G * a_w$
8. $E_a = 132.69 + 1.71 * G - 2.97 * a_w + 1.32 * a_w^2 + 0.88/(G + 2.5) + 0.60/(S + 2.5) - 1.44/(a_w + 2.5) - 0.89/(G * S) + 1.8/(G * a_w)$

G = Glucose (Code value)
a_w = Water activity (Code value)
S = Salt (Code value)
oil = Stripped corn oil (Code value)
pH = pH (Code value)

Log = Ten base logarithm
E_a = Apparent activation energy (kJ/mole)
k_{100} = Reference loss rate coefficient (1/min)

Table 6. Model prediction accuracy using various combinations of k_{100} and E_a equations

E_a	k_{100}	Equation 1	2	3	4	5	6
	r^2	0.87	0.91	0.82	0.91	0.88	0.82
7	Intercept	0.15	0.22	0.08	0.22	0.20	0.08
	slope	0.85	0.73	0.90	0.73	0.75	0.90
	r^2	0.84	0.91	—	0.91	0.89	0.67
8	Intercept	0.17	0.23	—	0.23	0.22	0.17
	slope	0.82	0.71	—	0.70	0.73	0.68

See Table 5

levels were plotted against the experimental response levels. A perfect model would have all points falling on a straight line intercepting the origin and have a slope of 1. Slightly positive intercepts and slopes

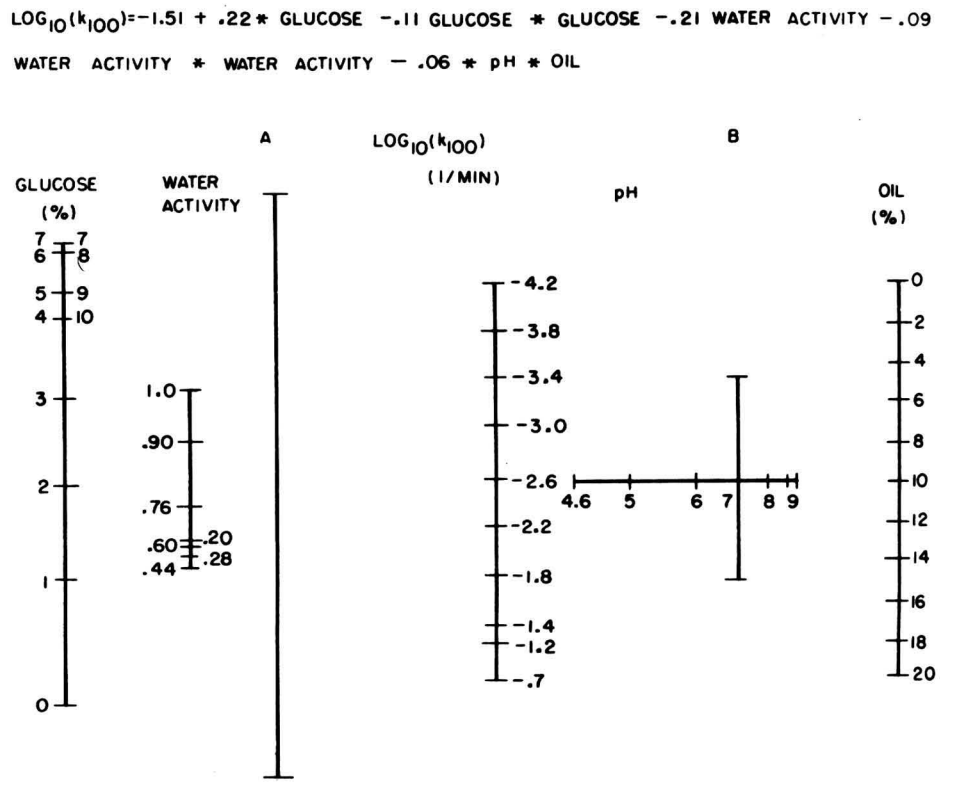

FIG. 3. NOMOGRAM USED TO DETERMINE THE PROTEIN LYSINE LOSS RATE COEFFICIENT AT 100C AS A FUNCTION OF INGREDIENT COMPOSITION

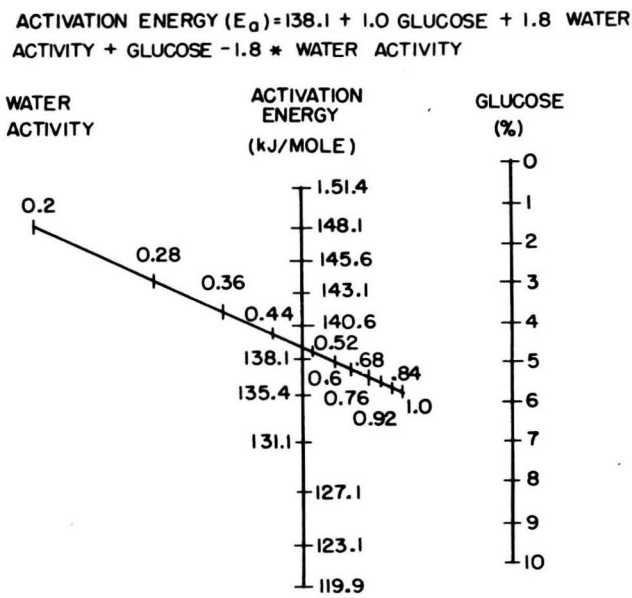

FIG. 4. NOMOGRAM USED TO DETERMINE ACTIVATION ENERGY AS A FUNCTION OF INGREDIENT COMPOSITION

somewhat less than 1 were noted in the verification tests. This is due to a bias inherent in regression procedures.

Nomograms for predicting k_{100} and E_a (Fig. 3 and Fig. 4) are provided to estimate the k_{100} and E_a values without a calculator. While these nomograms are not as accurate as the equations from which they are derived, they are a useful alternative.

The ten base log of k_{100} is found from Fig. 3 by locating the glucose, water activity, pH and oil levels on the respective scales. A straight line is passed through the glucose and water activity points and extended to line "A". Another line connects the oil and pH points and intersects the "B" line. A line connecting the "A" and "B" line intersections passes through the predicted $\log_{10}(k_{100})$ value on that scale.

The activation energy is found from Fig. 4. The water activity and glucose levels are located on the respective scales. A straight line connecting these points passes through the activation energy on the remaining scale.

These particular models have not been tested using different process procedures such as extrusion and baking where nonisothermal conditions and mixing occur. However, similar models developed to predict free lysine and free methionine losses under these conditions have successfully predicted losses (Wolf *et al.* 1981b).

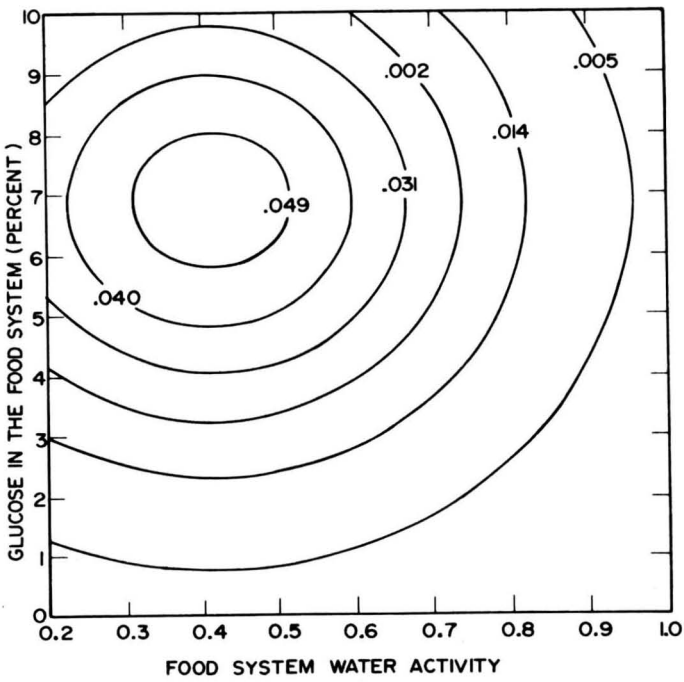

FIG. 5. PROTEIN LYSINE LOSS RATE COEFFICIENT AS INFLUENCED BY WATER ACTIVITY AND SUGAR

The successful k_{100} equations (Table 5) use a variety of terms in accounting for the variation in the loss rate coefficients. Linear and square terms for sugar demonstrate that there is a linear increase in the loss rate coefficient with increasing sugar until a saturation level of sugar occurs (Fig. 5). Note that the sugar level where this saturation occurs is greater than that employed in the previous sugar experiment. The effect of increasing water activity is inversely proportional to the loss rate coefficient, with the maximum loss rate occuring at a water activity near 0.4 (Fig. 5). These results reconcile the earlier results of Wolf *et al.* (1977) and Tsao *et al.* (1978) with those of Wolf *et al.* (1981). In the 1977 and 1978 papers, the authors were unable to show any significant role for water activity in protein-lysine losses at elevated temperatures (80-130 C). In the 1981 paper by Wolf *et al.*, the authors noted that maximum losses of free lysine containing model food systems occurred near 0.2 when elevated process temperatures were employed. Henderson and Perry (1976) have noted that in a closed biological system, water activity increased with temperature. Such an effect most likely occurred in these studies. Therefore, although the initial water activities were set from 0.2 to 0.9 at room temperature,

the effective range during processing may havc been significantly higher (0.5 to 0.95 for example). One inference that may be made from these results is that water activity levels wich provide for extended shelf-life may cause maximum protein lysine losses during processing at elevated temperatures.

Salt, pH and oil do not have a major effect on lysine losses relative to sugar and water activity. However, they do alter the loss rate coefficient and the best functioning equations include these terms. Salt, which occurs in a few k_{100} and E_a equations, has a negative influence on the loss rate coefficient. A possible explanation for the activity of salt has been discussed elsewhere (Wolf *et al.* 1981). Several of the empirical equations suggest that pH and oil have direct and indirect (interaction) effects on the loss rate coefficients. At low levels of oil, the effect of pH agrees with the literature (increasing pH increases the rate coefficient) regarding protein lysine losses. However, as oil concentrations increase beyond 10%, the equations suggest that increasing pH decreases the loss rate coefficient. This effect is causes by a pH-oil interaction term which occurs in several of the equations. Although there is no experimental evidence to directly prove that the interaction is occurring, it may be possible that at the processed temperatures used and at high oil concentrations there is enough hydrolysis occurring to produce critical levels of free fatty acids and a lowered pH.

The protein lysine loss models of Wolf *et al.* (1977) assumed that when soy protein isolates were processed in the presence of a reducing sugar, there were three phases to the loss curve; a first order loss phase, a transition phase (initiated at 55% loss) and a no loss phase. All three phases have been confirmed by Protein Efficiency Ratio studies (Wolf *et al.* 1979). However, the models used in this study do not assume the presence of a three phase loss curve, but rather a simple first order loss until the reactants are exhausted. This change in model assumption was made for the following reasons. The three phase loss curve only occurs in soy isolate model food systems which undergo a process with only minimal shear. In addition, these effects only occur in the simple model food systems (protein, sugar, cellulose). Adding a fatty acid to the base model food system or processing with extensive shear, such as occurs during extrusion, will cause the loss rate to follow a simple first order reaction.

The effect of extrusion on the lysine loss process suggests a possible explanation for the initiation of the transition and no loss phases in the model food systems discussed previously. It is believed that soy protein breaks down into its subunit structure before polymerizing during extrusion (Cumming *et al.* 1973). The near isothermal and extrusion processes have some similarities; however, they differ significantly in

the amount of shear applied to the food and consequently the protein. Without shear in the near isothermal non-stirred process, the protein may form a structure in which the lysine molecules are unavailable to sugar molecules. It is possible that the protein, in the absence of shear, polymerizes to protect lysine molecules from sugar molecules. The presence of oil may prevent the protein from forming a lysine protective structure.

CONCLUSIONS

These models for predicting protein lysine loss and the models for predicting free lysine and free methionine losses demonstrate the efficacy of the combined empirical-kinetic approach to model building and nutrient optimization. By adding transport models, which explain moisture, salt and heat transfer, the model will have an even greater application. There is also a need to expand the model to handle different salts, lipid oxidation and protein type. However, even without these suggested additions, the model can be an effective optimization tool for industrial processing.

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A NEW EMPIRICAL MODEL TO SIMULATE TRANSIENT SHEAR STRESS GROWTH IN SEMI-SOLID FOODS[1]

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ABSTRACT

A family of models has been developed which has the ability to simulate transient shear stress growth in foods. The models can be written as follows:

$$\tau = m(\dot{\gamma})^n \left[1 + (b_0 \dot{\gamma} t - 1)\frac{\sum b_i e^{-t/\lambda_i}}{\sum b_i}\right]$$

Three relaxation terms (seven parameters) are necessary to stimulate transient shear stress growth for stick butter, tub margarine and peanut butter at shear rates of 10 s^{-1} and 100 s^{-1}.

At small times the model tends to:

$$\tau = constant \cdot (b_0 \dot{\gamma} t)$$

which simulates the stress growth part of the curve. At long times the models tend to the power-law. The series of relaxation terms allows for the introduction of several time scales in the relaxation behavior of each food.

INTRODUCTION

Shear stress growth at inception of steady shear flow has frequently been used to characterize the transient rheology observed in most non-Newtonian fluid and semi-solid materials (Bird *et al.* 1977). Such experiments have also been conducted with fluid and semi-solid food materials (Elliot and Green 1972, DeMann *et al.* 1969, Szczesniak 1977, Kokini and Dickie 1981, Tiu and Boger 1974, Figoni and Shoemaker 1981). Stress overshoots are a result of such transient behavior and can

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range anywhere from 30% to 300% depending on the particular shear rate. These stresses must be estimated during shear processing of foods when sudden changes in shear rate occur. This is of particular importance when the relaxation time of the material is larger or comparable to the time scale of the experiment. It was recently shown that transient effects are also important in assessments of the textural attributes, spreadability (Kokini and Dickie 1982) and thickness (Dickie and Kokini 1983).

Several constitutive equations have been developed which predict different forms of transient shear stress growth. Some examples are the Bird-Carreau, the BKZ, the Bogue-Chen (1972), the Spriggs (1961) and the Zaremba-Fromm models. Among them, the Bogue-Chen model has been found to predict experimental data most closely in polymeric materials. Their use, in general, demands extensive numerical calculations.

Several first attempts have also been made to develop an equation capable of predicting transient shear stress growth in food materials. Elliot and Green (1972) have modeled transient shear stress growth in several foods assuming that these foods could be simulated by a Maxwell element coupled with a yield element. This analysis, although fundamentally very enlightening, does not account for nonlinear viscoelastic behavior frequently observed with most foods. It is nevertheless a first, very worthwhile attempt at explaining shear stress overshoots in materials which portray yield stresses such as foods.

Dickie and Kokini (1981) have attempted to simulate shear stress growth in fourteen foods using an empirical equation previously developed by Leider and Bird (1974). They found that the equation predicted peak shear stresses and peak times fairly well, but failed to predict transient decay accurately. Although the model was able to account for nonlinear behavior, one of its most serious shortcomings was a single exponential term to simulate the relaxation part of the curve.

In this work a new family of empirical models has been tested. These models are an extension of the earlier model developed by Leider and Bird and contain several relaxation terms:

$$\tau_{yx} = m(\dot{\gamma})^n \left[1 + (b_0 \dot{\gamma} t - 1)\frac{\sum b_i e^{-t/\lambda i}}{\sum b_i}\right]$$

where m, n power-law parameters
$\dot{\gamma}$ shear rate
t time
λ_i time constants
b_0, b_i constants.

The family of models provides many interesting features. First, the number of adjustable parameters can be increased at will to accommodate the wide spectra of relaxation times that can result from the complex nature of the foods studied. Second, regardless of the number of parameters involved, the model tends to the power-law model at long times since each $e^{-t/\lambda i}$ tends to zero making the term

$$(b_0 \dot{\gamma} t - 1)\frac{\sum b_i e^{-t/\lambda i}}{\sum b_i}$$

tend to zero. Third, when a single relaxation term is chosen the model reduces to the Bird-Leider equation. Finally, at short times ($t \simeq 0$) each $e^{-t/\lambda i}$ term tends to 1 and the equation reduces to:

$$\tau_{yx} = m(\dot{\gamma})^n \left[1 + (b_0 \dot{\gamma} t - 1)\frac{\sum b_i}{\sum b_i}\right]$$

which can be rewritten as:

$$\tau_{yx} = m(\dot{\gamma})^n (b_0 \dot{\gamma} t)$$

Since $m(\dot{\gamma})^n b_0 \dot{\gamma}$ is constant for each shear rate, this simulates the initial almost linear growth in shear stress with time. As time increases the exponential terms control the equation. The objective of this paper is to test the two and three relaxation term models. This effort concentrates on four foods: butter, margarine, peanut butter and canned frosting at shear rates of 10 s^{-1} and 100 s^{-1} where previous efforts with a single relaxation term model were inadequate.

MATERIALS AND METHODS

The transient shear stress data of stick butter, tub margarine, peanut butter, and canned frosting used in the analysis was that previously obtained by Dickie and Kokini (1981). The cone and plate geometry of the Rheometrics Mechanical Spectrometer was used and the transient shear stresses were measured at shear rates of 10 s^{-1} and 100 s^{-1}. All measurements were conducted at room temperature. The reader is referred to Kokini and Dickie (1981) for experimental details.

In order to simulate the experimental shear stress data a non-linear least squares procedure was used to obtain model parameters. This program may be obtained through Statistical Analysis Systems (SAS).

RESULTS AND DISCUSSION

Shear stress growth data as well as predictions of the 3 parameter, 5 parameter and 7 parameter models are shown in Fig. 1 through 7. The ordinate in all of these figures is the ratio of instantaneous shear stress to steady state shear stress and the abcissa is time in seconds. The solid lines on all figures are the experimental data. This data is compared with the predictions of the single relaxation term (three parameter) model, the two relaxation term (five parameter) model and three relaxation term (seven parameter) model. This comparison is offered for four of the foods which were not satisfactorily predicted by the Bird-Leider (three parameter) model. The results are shown in Fig. 1

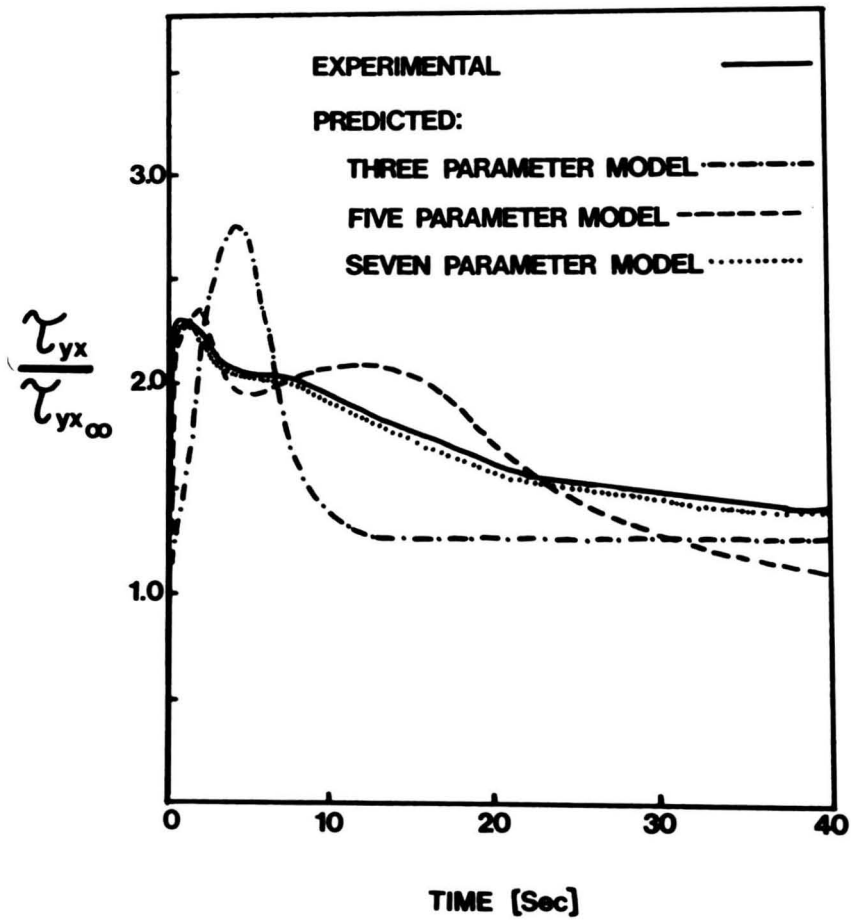

FIG. 1. SHEAR STRESS DEVELOPMENT OF STICK BUTTER AT $\dot{\gamma} = 10\ S^{-1}$

through 7 for stick butter, tub margarine and peanut butter at shear rates of 10 s^{-1} and 100 s^{-1} and for canned frosting at shear rate of 10 s^{-1}.

In Fig. 1 for stick butter at a shear rate of 10 s^{-1}, it can be seen that the new five parameter and seven parameter models predict shear stress growth better than the three parameter model previously tested (Dickie and Kokini 1981). The five parameter model develops oscillations. Although the fit has improved, a third relaxation term is necessary to accurately estimate transient shear stresses. The relaxation portion of the curve is well simulated and the seven parameter model offers a better estimate of peak overshoot and peak time.

The numerical values of the predictions are shown in Table 1. Transient data range from 0.25 to 140.0 s for a shear rate of 10 s^{-1}. This table clearly shows that the greatest improvement is in the relaxation portion of the curve. For example, at time equal to 20 s the new seven parameter model predicts a value of 421.0 Pascals, whereas the three parameter Bird-Leider model predicted a value of 244.6 Pascals. The experimental value is 435.2 Pascals. Predictions of shear stress overshoots and peak times are also greatly improved. The 7 parameter model predicts a peak shear stress of 640.7 Pascals at a time of 1.0 s while the experimental peak stress value is 626.3 Pascals at a time of .75 s. The 3 parameter model previously predicted a peak stress value of 755.3 Pascals at a time of 3 s.

In Fig. 2 experimental shear stress growth data and predictions of the three, five and seven parameter models are offered for stick butter at a shear rate of 100 s^{-1}. The five parameter model develops oscillations again while the seven parameter model simulates the transient shear stress curve closely. The estimated values are also much closer to the experimental values compared to the three parameter model. For example, it can be seen from Table 1 that in the relaxation part of the curve at time equal to 8 s, the three parameter model estimates a shear stress of 301.6 Pascals for an experimental shear stress of 473.4 Pascals; the new seven parameter model estimates a shear stress value of 482.4 Pascals. Peak shear stresses are also well estimated. The seven parameter model predicts a peak shear stress value of 762.75 Pascals at a time of 1 s for an experimental peak stress value of 790.74 Pascals at a time of 0.5 s.

In Fig. 3 shear stress growth data and predictions of the three models are shown for tub margarine at a shear rate of 10 s^{-1}. Again, both the five and seven parameter models simulate the shear stress growth data better than the three parameter as expected. The five parameter model displays oscillations as in the case of stick butter. Oscillations are also seen in the case of the seven parameter model, but they are not as

Table 1. Comparison of three parameter and seven parameter models for stick butter

	$\dot{\gamma} = 10s^{-1}$			$\dot{\gamma} = 100s^{-1}$		
Time (s)	τ_{exp}(Pa)	τ(3-Parameter)	τ(7-Parameter)	τ_{exp}(Pa)	τ(3-Parameter)	τ(7-Parameter)
0.25	265.8	186.2	323.0	518.0	382.4	543.4
0.50	541.5	336.3	504.4	790.7	617.4	687.5
0.75	626.2	455.8	598.6	722.1	750.0	749.7
1.00	622.3	549.5	640.7	675.8	812.9	762.7
2.00	604.9	739.1	625.5	607.2	744.0	649.6
3.00	594.7	755.2	584.1	579.7	566.5	542.5
4.00	582.9	697.2	570.3	550.6	438.4	494.6
5.00	573.0	615.7	567.8	528.3	365.5	480.4
6.00	561.2	534.7	565.2	504.2	328.1	479.2
7.00	551.4	464.1	559.1	490.5	310.0	481.1
8.00	543.5	406.8	549.4	473.4	301.5	482.3
9.00	533.7	362.2	537.2	463.1	297.7	481.7
10.00	525.8	328.5	523.7	452.8	296.0	479.2
20.00	435.2	244.5	421.0	375.6	294.7	408.3
40.00	374.1	242.3	379.2	320.7	294.7	316.2
60.00	344.6	242.3	349.1	291.6	294.7	297.8
80.00	307.2	242.3	317.2			
100.00				291.6	294.7	294.8
120.00	285.5	242.3	273.4			
140.00	275.7	242.3	261.4			

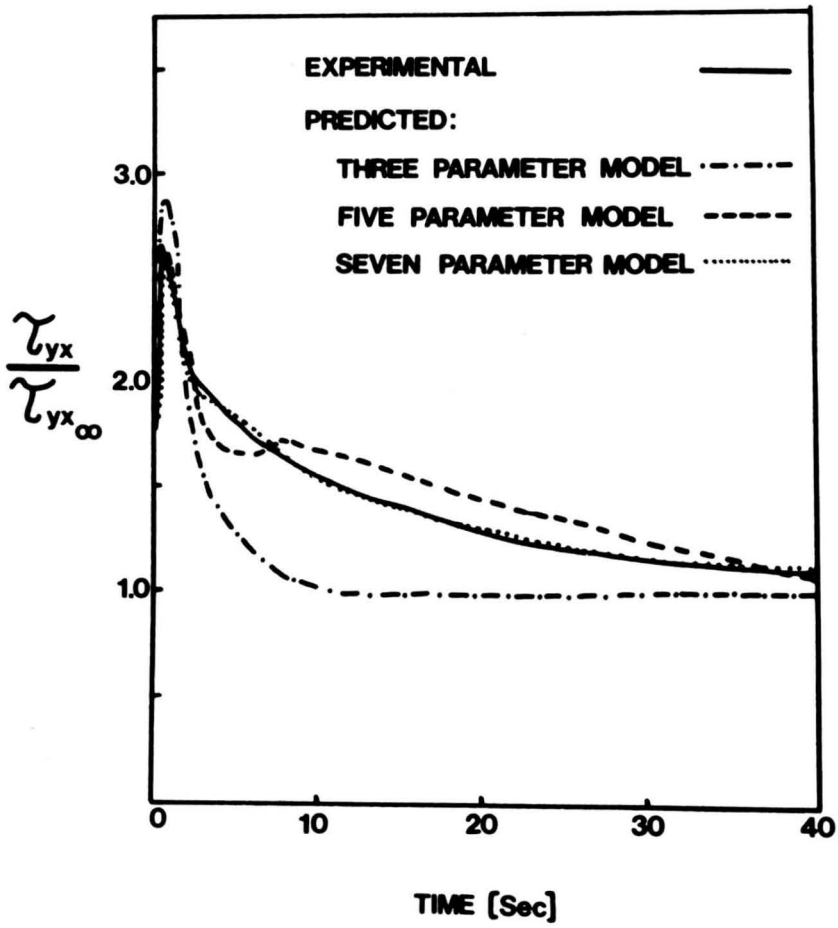

FIG. 2. SHEAR STRESS DEVELOPMENT OF STICK BUTTER AT $\dot{\gamma} = 100\ S^{-1}$

pronounced. In any case, the stresses in the growth and relaxation parts of the curve are well approximated by the seven parameter model. Peak stresses are approximated within 3.6% error as compared to 15% in the case of the three parameter model.

Experimental and predicted shear stresses for tub margarine at a shear rate of 100 s^{-1} are shown in Fig. 4. It can be seen again that both of the new models describe the experimental shear stresses more accurately than the three parameter model of Bird and Leider. The relaxation portion of the curve is well simulated again and the seven parameter model offers the best estimate of peak overshoot and peak time.

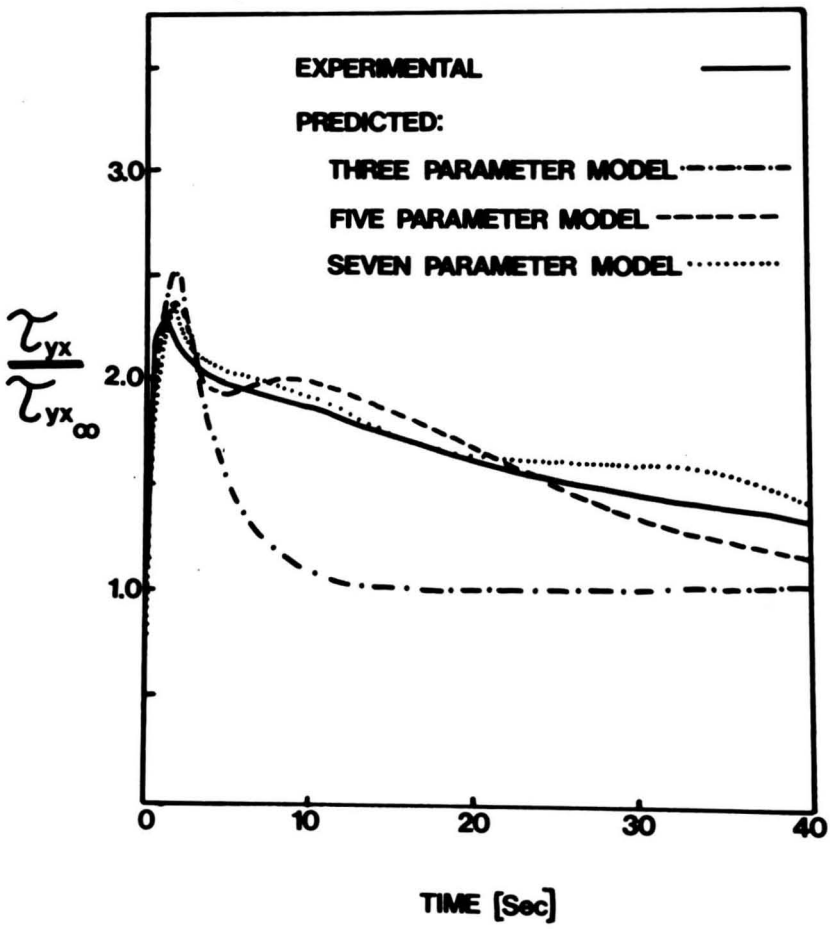

FIG. 3. SHEAR STRESS DEVELOPMENT OF TUB MARGARINE AT $\dot{\gamma} = 10\ S^{-1}$

In Fig. 5 and 6 similar observations can be made for peanut butter at shear rates of 10 s^{-1} and 100 s^{-1}. At both shear rates the seven parameter offers the best estimate of transient shear stresses.

Lastly, in Fig. 7 for canned frosting at a shear rate of 10 s^{-1}, unlike all the previous foods studied, shear stress data is inaccurately estimated by all three models. Both the five and seven parameter models, although an improvement over the three parameter model, do oscillate considerably and are comparatively unsatisfactory.

The estimated parameters are shown in Table (2) and Table (3). Table (2) contains estimates of the five parameter model and Table (3) contains estimates of the seven parameter model. It can be seen from

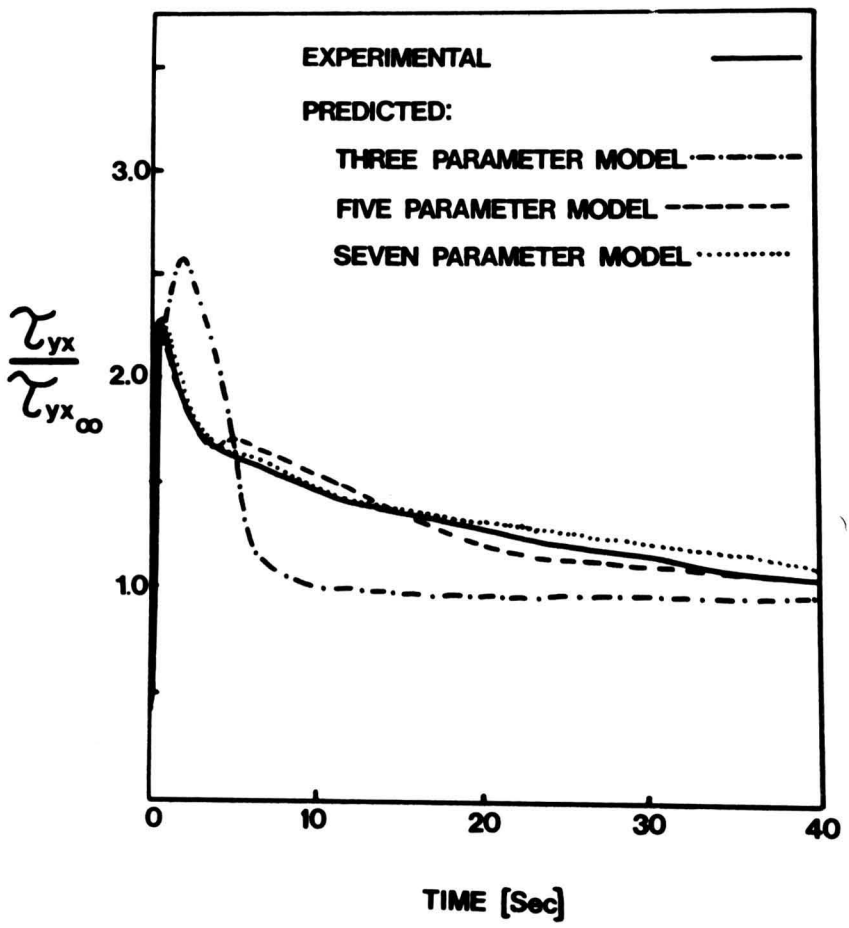

FIG. 4. SHEAR STRESS DEVELOPMENT OF TUB MARGARINE AT $\dot{\gamma} = 100\ S^{-1}$

the tables that b_0 values are very similar for both the five and seven parameter models. This is indeed expected since the value of b_0 is independent of the number of relaxation terms in the model. What is unexpected is the fact that λ_1 values are also very close for both the five and seven parameter models. b_0 values decreased with increasing shear rate for peanut butter, stick butter, and tub margarine. No material inference can be drawn from this increase since the value of b_0 is not only a function of the shear rate but also a result of the equilibrium shear stress reached at that viscosity.

The family of models portrays the same features offered by the single relaxation term model previously developed by Leider and Bird; that is,

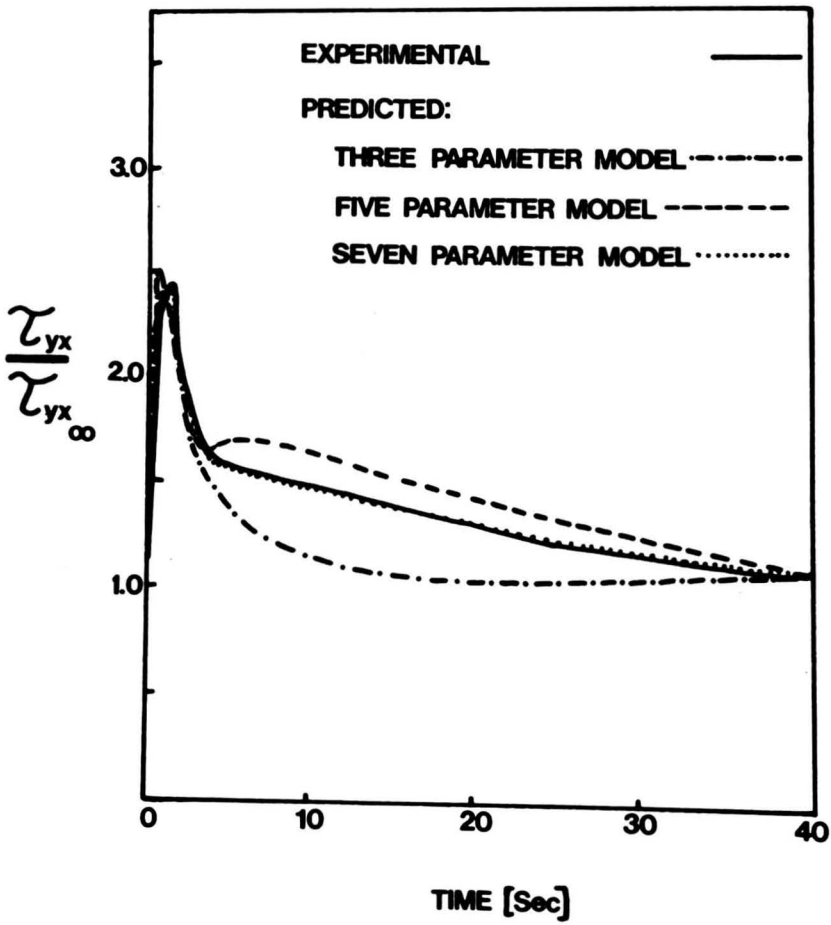

FIG. 5. SHEAR STRESS DEVELOPMENT OF PEANUT BUTTER AT $\dot{\gamma} = 10\ S^{-1}$

the models incorporate the initial elastic response in the $\dot{\gamma}t$ term. At very small times and at a constant shear rate the model reduces to:

$$\tau = \text{constant} \cdot (b_0 \dot{\gamma} t)$$

where $\dot{\gamma}t$ is equal to the total strain the material is subjected to.

In the relaxation part of the equation each constant $b_i/\sum b_i$ assigns a weight to the ith exponential relaxation term. The relaxation term with the largest $b_i/\sum b_i$ controls the relaxation behavior until the exponential term associated with it decays to relatively small values. This term must therefore have a comparatively small λ value if the other terms are to contribute. Indeed, a close look at the tables shows

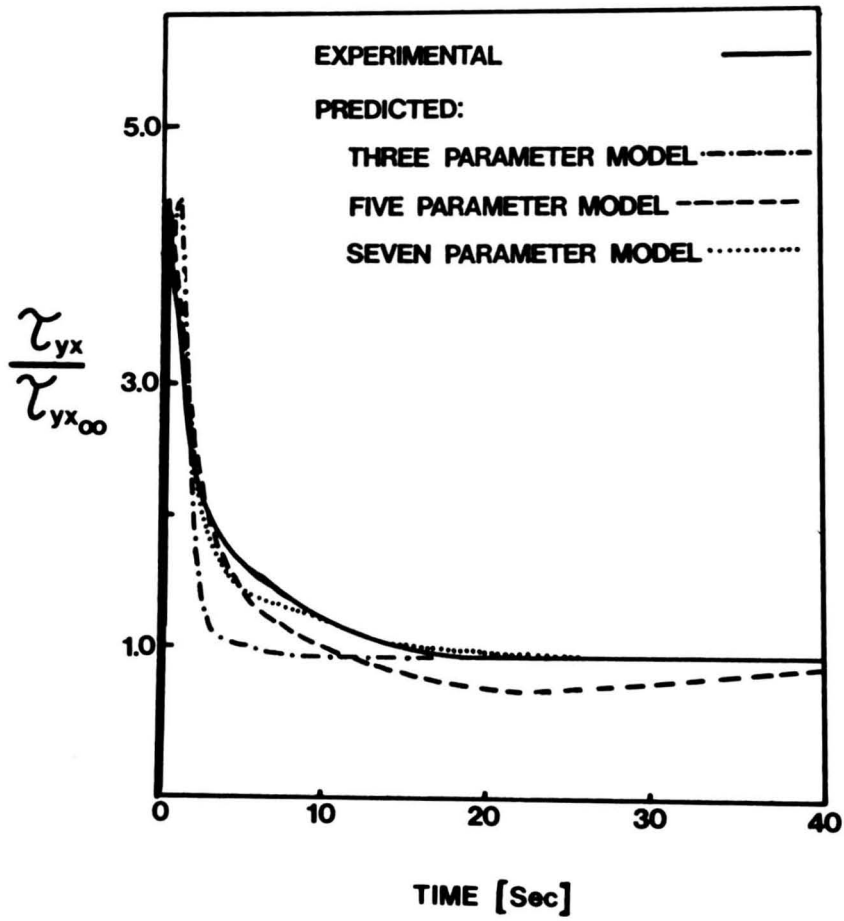

FIG. 6. SHEAR STRESS DEVELOPMENT OF PEANUT BUTTER AT $\dot{\gamma} = 100\ S^{-1}$

that for all foods at all shear rates this is the case for both the five and seven parameter models. Conversely, the largest λ_i values are associated with the smallest $b_i/\sum b_i$ values.

Each λ is similar conceptually to a Maxwell relaxation time and consequently λ can be regarded as a relaxation time. The longest relaxation times are 25.49 s and 8.91 s for peanut butter at shear rates of 100 s^{-1} and 10 s^{-1}, respectively. Those for stick butter are 31.12 s and 8.93 s for shear rates of 10 s^{-1} and 100 s^{-1}, respectively. For tub margarine the largest λ values are 18.29 and 21.68 s for shear rates of 100 s^{-1} and 10 s^{-1}, respectively, and finally the longest relaxation time is 7.5 s at a shear rate of 10 s^{-1}.

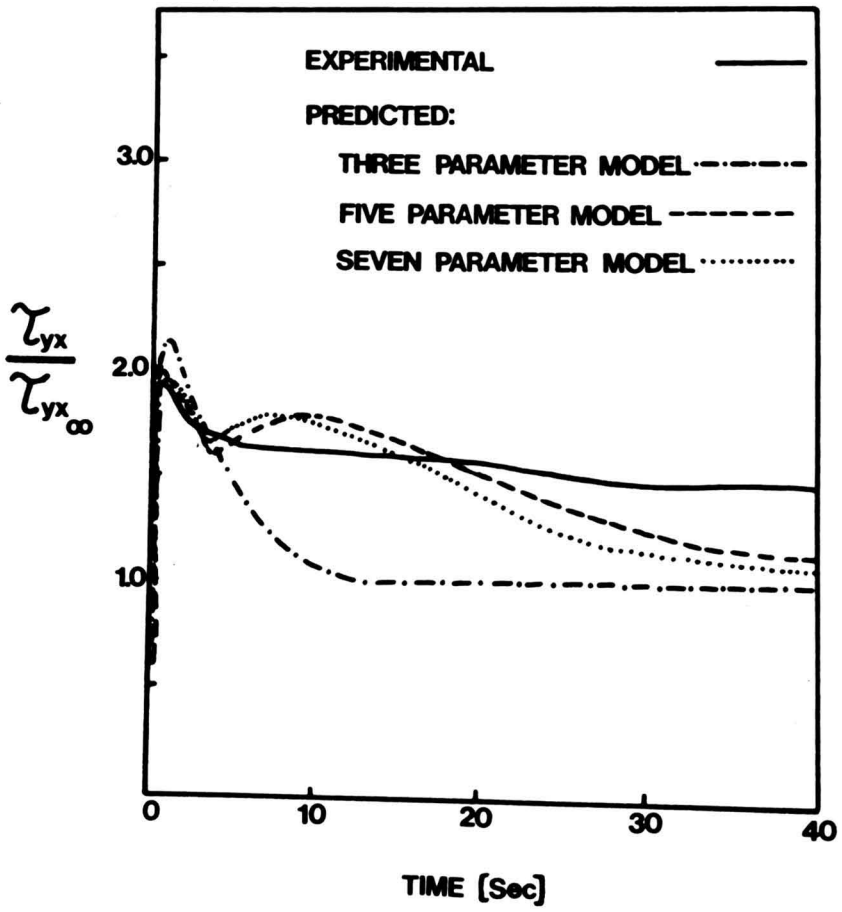

FIG. 7. SHEAR STRESS DEVELOPMENT OF CANNED FROSTING AT $\dot{\gamma} = 10\ S^{-1}$

Considering that the model is empirical in nature it contains some of the basic elements of constitutive equations. For example, the Spriggs and Bird-Carreau models contain series of exponential terms which are a function of several material parameters. These models result from structural assumptions during flow. For example, the Bird-Carreau model (1972) is a result of molecular network theory to explain the behavior of rubber-like solids (Christiansen and Leppard 1974). When the assumption is made that crosslinks are only temporary, the theory can be extended to viscoelastic liquids. Clearly no structural assumptions of this nature have been made in this study and the equations developed are only extensions of an earlier empirical model to simulate predictions of the Zaremba-Fromm model (Leider and Bird 1974), a corotating Maxwell model.

Table 3. Empirical constants for seven-parameter model

	b_0	b_1	b_2	b_3	λ_1	λ_2	λ_3
Peanut Butter							
$\dot{\gamma} = 10s^{-1}$	0.65	0.10	2.72	1.00	8.91	0.57	1.07
$\dot{\gamma} = 100s^{-1}$	0.14	25.49	0.01	0.74	0.61	15.81	3.64
Stick Butter							
$\dot{\gamma} = 10s^{-1}$	0.58	5.98	0.06	0.74	0.79	31.10	4.89
$\dot{\gamma} = 100s^{-1}$	0.10	0.33	2.14	21.60	8.93	2.12	0.42
Tub Margarine							
$\dot{\gamma} = 10s^{-1}$	0.43	0.03	0.25	1.96	21.68	4.34	0.80
$\dot{\gamma} = 100s^{-1}$	0.07	8.05	0.05	0.60	0.53	18.29	3.30
Canned Frosting							
$\dot{\gamma} = 10s^{-1}$	0.47	0.07	0.45	0.80	7.50	0.77	0.55

Table 2. Empirical constants for five-parameter model

	b_0	b_1	b_2	λ_1	λ_2
Peanut Butter					
$\dot{\gamma} = 10s^{-1}$	0.74	0.03	0.90	7.95	0.58
$\dot{\gamma} = 100s^{-1}$	0.14	4.26	0.30	0.60	2.23
Stick Butter					
$\dot{\gamma} = 10s^{-1}$	0.54	1.67	0.12	0.95	9.82
$\dot{\gamma} = 100s^{-1}$	0.10	1.47	0.10	0.47	3.93
Tub Margarine					
$\dot{\gamma} = 10s^{-1}$	0.42	0.10	1.30	8.59	0.92
$\dot{\gamma} = 100s^{-1}$	0.07	0.28	0.02	0.57	5.63
Canned Frosting					
$\dot{\gamma} = 10s^{-1}$	0.47	0.08	−6.21	0.88	0.88

CONCLUSIONS

The model is useful in several ways:

i) the restriction imposed by a single relaxation term has been removed by the addition of series of relaxation terms,
ii) multiple relaxation terms are more realistic in terms of portraying the relaxation behavior of nonhomogeneous food materials,
iii) the models are also able to converge to the powerlaw at steady state.

One of the most important shortcomings of the model is the lack of any relationship between each parameter and shear rate. It should be possible, however, to generate functions of shear rates for each parameter once stress growth functions at several shear rates have been obtained. Such functions are beyond the scope of this study.

A second limitation of this study is the lack of any attempt to relate parameters to structural information about each food. Nevertheless, the development of an empirical equation capable of simulating stress growth development is an improvement over available models in reference to food materials. It is one of the purposes of this laboratory to attempt to develop constituitive equations in the future which should lead to the empirical equation obtained in this study.

ACKNOWLEDGMENTS

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A MATHEMATICAL MODEL TO MONITOR PRODUCT LOSSES DURING FOOD PROCESSING[1]

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INTRODUCTION

The opportunities for improvement in efficiency of raw food product utilization are significant when considering the magnitudes of raw product that are not a part of the primary product reaching the consumer. As indicated by Heldman (1979), losses and/or wastes may be as much as 40 to 60% of the raw commodity when considering food products such as potatoes, beef or apples. Although portions of these losses and/or wastes must be considered intentional, there have been limited attempts to increase magnitudes of raw materials within the primary product or evaluate alternate uses of the waste streams from food processing.

The feasibility of reduction of losses and/or wastes from food processing has improved significantly in the past few years due to two factors: (a) rapidly increasing costs of energy and (b) increased costs for treatment of waste streams. Costs of energy influence the value of the product at all stages in the food chain and provide justification for recovery of product components that might normally appear in a waste stream. Nearly simultaneously, the laws associated with maintaining water quality have resulted in major adjustments in the cost of waste treatment. By considering both factors, the feasibility of reducing losses and/or wastes as well as recovery of components from waste streams have become popular alternatives for the food industry.

Although mathematical models have become an important component of process analysis in all phases of industrial research, the use of

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models for monitoring processes has had limited applications in food industry. The application being proposed in this manuscript would suggest the use of mathematical models as tools for decision-making when considering the feasibility of loss and/or waste reduction technologies. Proper formulation of the model should lead to identification of locations of maximum product loss and the development of the feasible technologies for assuring that maximum quantities of important product components are in primary product streams.

The magnitudes of losses and/or wastes from food processing operations have been summarized by Heldman (1979) and Heldman (1981). These reports indicate that losses from primary product streams are approximately 52% for potato processing, 40% for fresh beef, 50% for apple processing and 3.5% for milk processing. The locations of maximum product loss have been identified for each commodity with peeling and cutting operations contributing most to losses during potato and apple processing. The major losses associated with fresh beef handling are identified as cutting and trimming operations. Processing operations (pasteurization and storage) contribute most to the relatively small losses during milk processing. Although these results tend to indicate locations where losses are large, the most appropriate steps to be initiated in a loss reduction program can be achieved through a mathematical analysis.

The objectives of the analysis to be presented include: (1.) To develop a mathematical model to describe magnitudes of product losses during food processing. (2.) To illustrate the use of the mathematical model through application to operations associated with a specific food commodity, and (3.) To evaluate the feasibility for reduction of food losses and/or wastes during food processing using the mathematical model.

MODEL DEVELOPMENT

A mathematical description of product losses in a sequence of processing operations requires several unique features: (1.) The model should provide the ability to monitor important product components at all stages in a sequence of operations. (2.) The description must include the capability to incorporate factors to account for characteristics of each conversion process, and (3.) The model should lead to a point where losses at given locations in a sequence can be minimized and/or resource recovery can be optimized.

The proposed model is developed in a general manner for a sequence of n operations as illustrated in Fig. 1. As presented, the model describes individual conversion operations involving a food commodity

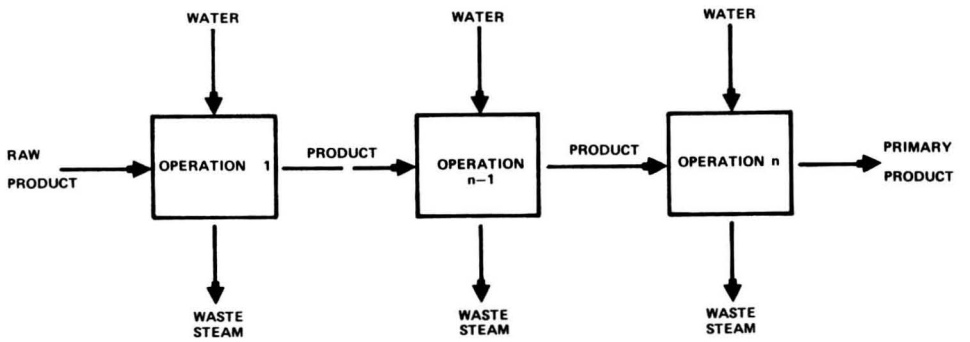

FIG. 1. SCHEMATIC ILLUSTRATION OF THE SEQUENCE OF FOOD PROCESSING OPERATIONS

and water. For whatever pupose, the product and water are brought into contact during the operation and leave the operation in separate streams. The model describes or monitors the quantities of product that are leaving with the loss stream and not with the primary product stream. The proposed description would allow for several input streams and/or monitoring of several individual product components. In this model, the term "stream" does not imply a liquid stream, but the flow of any material associated with the operation being considered.

The proposed model utilizes a conversion matrix for each operation. The matrix for operation k would be:

$$T_k = \begin{bmatrix} t_{11} & t_{12} \cdots t_{1m} \\ t_{21} & t_{22} \cdots t_{2m} \end{bmatrix} \tag{1}$$

where

t_{1j} = the product converted through the operation, kg of output component/kg of product in.
t_{2j} = process water converted through the operation, kg of output component/kg of water in.
m = number of components monitored.
n = number of operations.

for:

$j = 1,2,\ldots,m.$
$k = 1,2,\ldots,n.$

As indicated by the definitions of the $t_{i,j}$, the first row gives the per unit contribution of input product to each output stream being monitored—this includes product streams and waste streams.

The second row gives the per unit contribution of input water to each output stream being monitored.

The second matrix required for the model is an input matrix defined as:

$$S_k = [s_1 \quad s_2] \tag{2}$$

where

s_1 = total mass of product into operation
s_2 = total mass of water into operation

By multiplication of the two matrices, the total output of each component from the operation is obtained. For example, a two component system would be described by:

$$P = S_k \times T_k = [s_1 \quad s_2]\begin{bmatrix} t_{11} & t_{12} \cdots t_{1m} \\ t_{21} & t_{22} \cdots t_{2m} \end{bmatrix} \tag{3}$$

$$P = [(s_1 t_{11} + s_2 t_{21}) \quad (s_1 t_{12} + s_2 t_{22}) \cdots (s_1 t_{1m} + s_2 t_{2m})]$$

where:

$$s_1 t_{1j} + s_2 t_{2j} = \text{total mass of output stream } j. \tag{4}$$

In order to use the proposed model to monitor product loss, the outputs from at least two matrix multiplications must be compared. The first can be referred to as *Perfect Technology*:

$$P^B = S \times T^B \tag{5}$$

where the output would represent maximum possible conversion of input product to primary product as output. The second output would be the *Actual Technology* with:

$$P^A = S \times T^A \tag{6}$$

and an output representing the actual conversion of product components to primary product. By computation of the difference between the Perfect Technology (P^B) and the Actual Technology (P^A), the losses associated with a given operation are established:

$$\text{Losses} = P^B - P^A \tag{7}$$

The sequential computation of losses as reflected in the reductions of product quantities from one operation to another provides the basis for monitoring product losses in a series of operations. Assuming the appropriate conversion coefficients are known or can be measured, the proposed model will allow monitoring of several product components as the product is converted from raw material to a final primary product.

APPLICATION OF THE MODEL

As indicated by Heldman (1981), potato processing operations involve numerous individual stages and significant magnitudes of product loss. More recent analysis indicates that the manufacturing of frozen french fries and similar potato products can be described by twelve (12) separate steps where product modifications require water use and corresponding product loss. These operations are described in Table 1. As illustrated, each stage is required to assure that the desired product will be produced by the sequence of operations.

The results in Fig. 2 illustrate the magnitudes of product loss at several of the operations. As is evident, the peeling, trimming and sizing operations are major contributors to the total loss of 36.6 kg product/100 kg raw product entering the system. Another significant loss is a part of the liquid effluent which contains product solids from several sources. The composition of the various waste streams will vary depending on the source as indicated by Fig. 3. A major portion of the total waste stream is identified as alcohol-insoluble solids (22.61 kg/100 kg product solids) while much smaller components are ash and alcohol soluble solids. Reducing sugars were a nearly insignificant portion of the total waste stream. As would be expected, ash was the largest proportion of the silt waste stream. The waste stream from the trimming and sizing operations contained significant amounts of alcohol-insoluble solids indicating that portions of potato tubers in the waste streams are contributing to the starch losses.

Table 1. Operations involved in processing of frozen french fries and similar potato products

Operation	Description
1. Sorting	Removal of visibly unacceptable raw potato tubers.
2. Silt removal	Washing of potato tubers to remove major portions of soil.
3. Cleaning	Additional cleaning of potato tubers.
4. Peeling	Use of steam or other agents to remove peel from tuber.
5. Scrubber-Washer	Cleaning of potato tuber after peeling.
6. Trimming	Manual removal of unacceptable tubers or tuber portions.
7. Cutting	Cutting the potato tubers into portions desired for final product
8. Sizing	Removal of tuber portions that may be too small or too large.
9. Blancher I	First stage of operation for enzyme inactivation and texture improvement.
10. Blancher II	Second stage of operation to assure low bacterial count and desired color.
11. Dry Handled Waste	An accumulation of product solids from several previous stages.
12. Miscellaneous	Additional product losses unaccounted for in other stages.

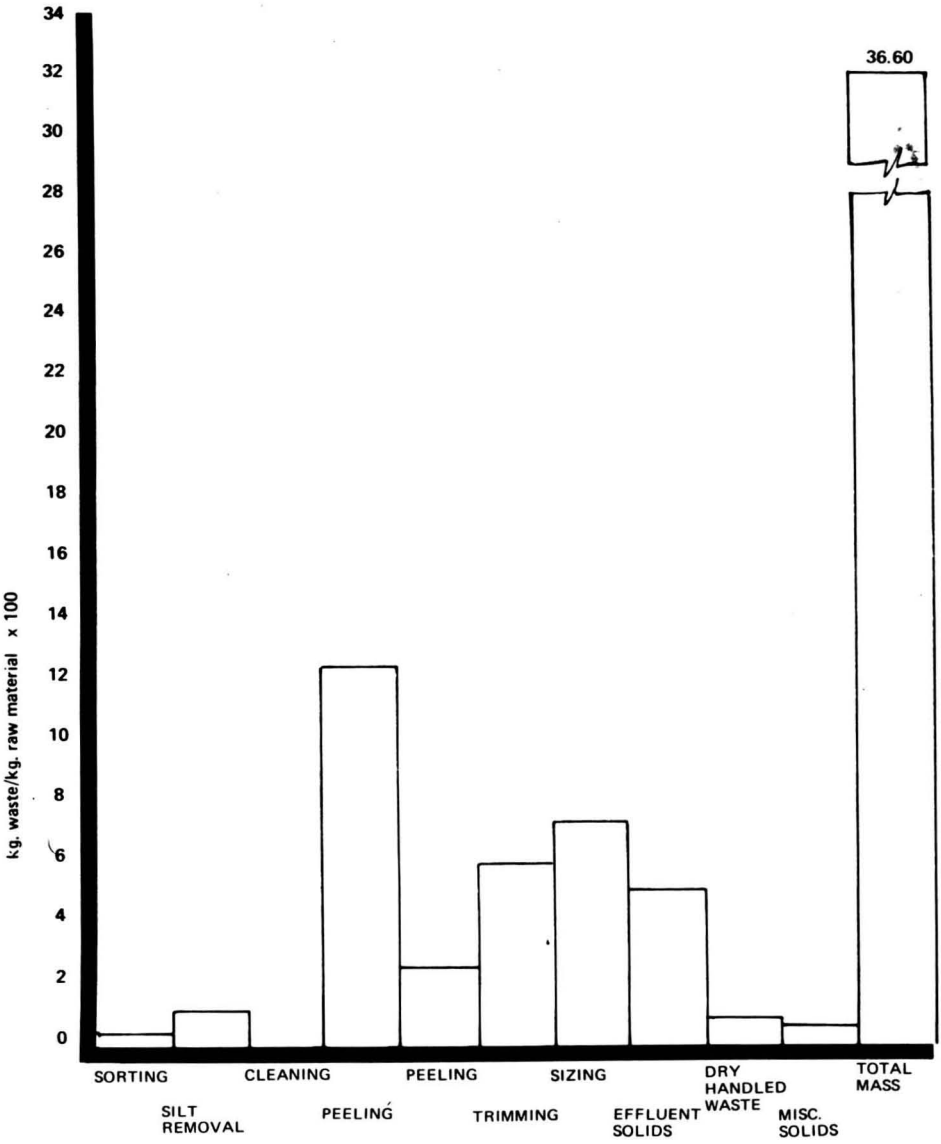

FIG. 2. MAGNITUDES OF PRODUCT LOSS FOR UNIT OPERATIONS FOR POTATO PROCESSING

In order to apply the proposed model to the potato operations described in Figure 3, specific input information is required. Data collected for Figure 3 along with water usage data presented by Shirazi (1979) have been used to develop Table 2. Based on data provided and mass balance on each operation, input values for the conversion matrix

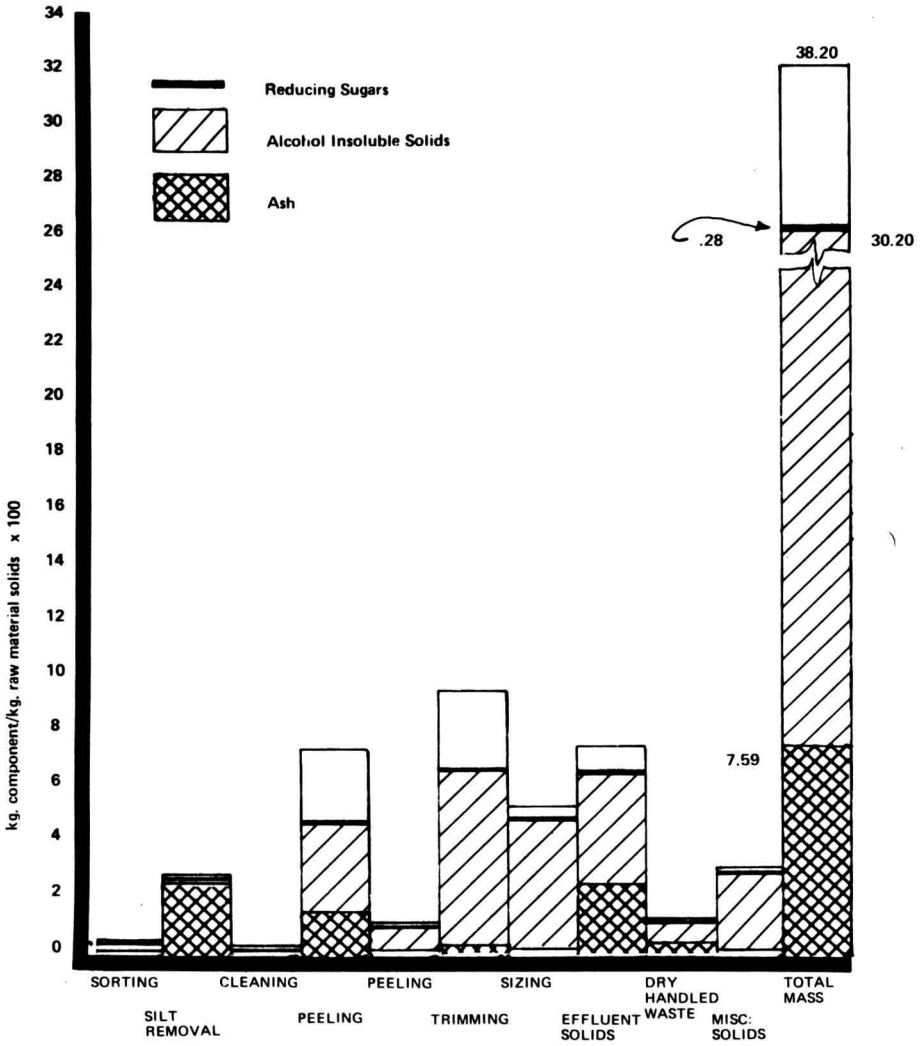

FIG. 3. COMPOSITION OF WASTE STREAMS FROM UNIT OPERATIONS FOR POTATO PROCESSING

have been computed. For this example, the product composition has been treated as two components whereas the model can be used for an unlimited number of product components.

The output streams to be monitored are total product, waste stream, potato solids and product water. The resulting matrix $P = [p_1 \quad p_2 \quad p_3 \quad p_4]$ will be in output units. p_3, for example will be in kilograms of potato solids out. Other outputs (such as starch) could be monitored as

Table 2. Product loss and water usage for processing of frozen french fries and similar potato products

Operation	Water Usage (kg H_2O/kg prod)	Waste Stream Solids (kg solids/kg solids)	t_{11} (kg prod/kg prod)	t_{12} (kg prod/kg H_2O)
Sorting	1.445×10^1	4.5×10^3	0.9955	4.4795×10^3
Silt removal	4.37×10^2	2.89×10^2	0.9711	2.8916×10^2
Cleaning	2.08×10^2	1.0×10^3	0.9990	9.9424×10^4
Peeling	3.844×10^1	8.43×10^2	0.9158	8.4184×10^2
Scrubber-Washer	8.684×10^1	9.07×10^9	0.9999	1.0×10^8
Trimming	4.21×10^2	9.4×10^2	0.9060	9.3967×10^2
Cutting	2.578×10^1	2.07×10^8	0.9999	1.0×10^8
Sizing	1.974×10^1	5.28×10^2	0.8130	1.8696×10^1
Blanching I	4.931×10^1	8.77×10^{10}	0.9999	1.0×10^8
Blanching II	7.018×10^1	5.60×10^{10}	0.9999	1.0×10^8
Dry Handled Waste	1.0×10^2	1.09×10^2	0.9891	1.09×10^2
Miscellaneous	9.042×10^1	2.98×10^2	0.9698	3.02×10^2

well. An advantage of the model is that it does not require the output streams to be mutually exclusive.

Application of the model requires computation for Perfect Technology using Eq. (5). In such a case, all inputs are converted but no input quantities are converted to waste streams, as indicated by the following matrix for the trimming operation:

$$P^B = [100 \quad 4.21] \times \begin{bmatrix} 1.0 & 0 & .225 & .775 \\ 0 & 1.0 & 0 & 0 \end{bmatrix}$$

$$= [100 \quad 4.21 \quad 22.5 \quad 77.5]$$

This computation indicates that the composition of the potato (22.5% solids, 77.5% water) is maintained during the conversion process. The input matrix was set up using 100 kg product in and 4.21 kg water as obtained from Table 2. The output matrix indicates that 22.5 kg product solids have been preserved and the total quantity of water leaving is 81.71 kg. This quantity of water includes 77.5 kg in the product and 4.21 kg water provided for the conversion process.

The use of the model for the actual technology of the process requires recognition that the model assumes conservation of mass and that losses are reflected in transfer of product solids from primary product to liquid waste streams. It follows that:

$$P^A = [100 \quad 4.21] \times \begin{bmatrix} .90603 & .09397 & .20399 & .70205 \\ 0 & 1 & 0 & 0 \end{bmatrix}$$

$$= [90.603 \quad 13.607 \quad 20.399 \quad 70.205]$$

where matrix (T) input ($t_{11}, t_{12}, t_{13}, t_{14}$) are computed from trimming operation values given in Table 2. The output streams to be monitored are total product, waste stream, potato solids and product water. The resulting matrix $P = [p_1 \quad p_2 \quad p_3 \quad p_4]$ will be in output units. p_3, for example will be in kilograms of potato solids out. Other outputs (such as starch) could be monitored as well. An advantage of the model is that it does not require the output streams to be mutually exclusive. Losses are then computed as $P^B - P^A = [9.397 \quad -9.397 \quad 2.1134 \quad 7.2833]$. The second entry indicates that the waste stream "loss" is negative. This means that the waste stream became more massive by absorbing product losses. (In this case a negative loss is a gain in waste.)

The values of conversion matrix components as well as magnitudes of solids and product loss for each of the twelve potato processing operations is presented in Table 3. As is evident, the magnitudes of the

Table 3. Product losses computed from conversion matrix for processing of frozen french fries and similar potato products

Operation	t_{13} (kg solids/kg prod)	t_{14} (kg H_2O/kg prod)	Solids Loss (kg solids/kg prod)	Product Water Loss (kg H_2O/kg prod)
Sorting	0.2240	0.7715	1.0115×10^3	3.468×10^3
Silt removal	0.2185	0.7526	6.4982×10^3	2.2318×10^2
Cleaning	0.2248	0.7742	2.2464×10^4	7.696×10^4
Peeling	0.2062	0.7097	1.8836×10^2	6.5348×10^2
Scrubber-Washer	0.2251	0.7749	0.0	0.0
Trimming	0.2040	0.7020	2.1134×10^2	7.2833×10^2
Cutting	0.2251	0.7749	0.0	0.0
Sizing	0.1831	0.6299	4.2066×10^2	1.4489×10^1
Blanching I	0.2252	0.7748	0.0	0.0
Blanching II	0.2252	0.7748	0.0	0.0
Dry Handled Waste	0.2227	0.7664	2.45×10^3	8.45×10^3
Miscellaneous	0.2185	0.7513	6.6911×10^3	2.3509×10^3

coefficients $(t_{11}, t_{12}, t_{13}, t_{14})$ vary significantly with operation. The lower quantity coefficients are associated with operations having more significant product losses as indicated by additional data presented on the table. The solids loss and product loss values should be viewed as quantities needed to compensate for losses with recognition that the type of solids or product required to replace losses will change with location in the sequence of operations. For example, losses during sorting or cleaning can be replaced by raw products, while losses during sizing must be replaced by potatoes or potato solids in the same condition as those that are lost at this point in the sequence.

Another use of the proposed model would be in a sequence of operations using the coefficients and matrices to compute outputs from each operation. The first operation would appear as:

$$P^A = [100 \quad 14.45] \times \begin{bmatrix} .99552 & .0044795 & .22399 & .77153 \\ 0 & 1 & 0 & 0 \end{bmatrix}$$

$$= [.99552 \quad .14898 \quad 22.399 \quad 77.153]$$

indicating that all product solids and water entering the first operation (sorting) have been accounted for. Using the fact that 0.45 kg product/100 kg product in have been lost in the first operation, the second operation (silt removal) would be:

$$[99.552 \quad 4.3504] \times \begin{bmatrix} .97108 & .028916 & .21850 & .75259 \\ 0 & 1 & 0 & 0 \end{bmatrix}$$

$$= [96.673 \quad 7.2291 \quad 21.752 \quad 74.921]$$

This indicates the actual yield of product and other output streams after two successive operations on 100 kg of product.

In addition to the monitoring of solids losses and product losses and the ability to identify quantities and types of product required to compensate for losses, the proposed model can be used to evaluate factors influencing magnitudes of losses. By varying the water usage to individual operations, the influence on losses can be evaluated as a first step in determining operations deserving more in-depth analysis. In addition, the impact of feasible reductions in waste stream solids could be evaluated efficiently.

The proposed model has two additional characteristics that would be useful in evaluating potential for reduction of product losses. The model has the capability to incorporate a complete array of product components. This allows monitoring of all product components and the possibility of selecting operations for more detailed analysis on the

basis of specific component recovery. The second characteristic of the model is the ability to incorporate optimization. This step would allow more detailed analysis of alternatives that might result in more effective utilization of raw product resources.

CONCLUSIONS

1. A mathematical model incorporating a conversion matrix and an input matrix has the capability to monitor product components during typical food processing operations.
2. Applications of the proposed mathematical model to potato processing operations leads to computation of coefficients for the input matrix from typical water usage and solid loss data.
3. The proposed model is capable of monitoring product losses in a sequence of operations and allows for evaluating loss reduction potential.
4. The potential for monitoring all product components through a sequence of operations is possible with the model along with the opportunity for optimization of product solids recovery.

ACKNOWLEDGMENT

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LITERATURE ABSTRACTS

ABSTRACTS FROM JOURNAL OF FOOD SCIENCE

Moisture Equilibrium in Apples at Several Temperatures: Experimental Data and Theoretical Consideration. G.N. Roman, M.j. Urbicain, E. Rotstein. J. Food Sci. *47*, 1484-1488 & 1507.

Moisture equilibrium data for desorption of water from apples was determined at 20°, 30°, 40°, 50° and 60°C. The rehydration 40°C isotherm was also found. The experimental procedure was a gravimetric dymanic method. Sorptive capacity decreases as temperature increases. Rehydration of the dried material results in hysteresis. The data are interpreted in thermodynamic terms. Specific surface and monolayer concentrations are also found. Pore size distribution studies show that the most frequent pore radii at 20°C and 40°C are, respectively, 26 Å and 22 Å. Hysteresis data are compared with what would be expected from the cellulose wall, indicating that solubility and other effects increase sharply the sorptive capacity of the fruit. A comparison of desorption and adsorption characteristics shows that dehydration results in serious damage of the fruit structure.

Prediction of Sorptional Equilibrium Data for Starch Containing Foodstuffs. G. H. Crapiste, E. Rotstein. J. Food Sci. *47*, 1501-1507.

Water accounting in a foodstuff can be done using water chemical potential to describe the equilibrium. Inspection of the structure of typical potato tissue leads to recognition of its intervening phases. Considering the chemical potential of water at each phase the corresponding amount of water can be predicted. Using these expressions and typical composition, the equilibrium water content of the foodstuff can be predicted with good agreement with experimental data. A number of correlations have been studied, concluding that the approach presented is the only one providing a good representation in the entire range of moisture contents. The method is extended to beans, white rice, peas and corn.

Effect of Chlorine Treatment on Wheat Flour and Starch: Measurement of Thermal Properties by Differential Scanning Calorimetry. J.F. Allen, J.W. Sherbon, B.A. Lewis, L.F. Hood. J. Food Sci. *47*, 1508-1511.

Differential scanning calorimetry (DSC) was used to study the effect of chlorine treatment of wheat flor on the heat of gelatinization of the wheat flour and starch. The DSC thermograms were corrected for heat capacity changes and thermal lag. An endothermic transition occurred in both flours and starches at a temperature commonly associated with starch gelatinization. The enthalpy (Δ H) for the starches was concentration dependent. The chlorine treatment did not affect significantly the transition temperatures nor enthalpies of either the flour or the starch isolated from it. Addition of sucrose delayed the onset of gelatinization and increased the Δ H for both treated and untreated wheat flours and starches.

Journal of Food Process Engineering 6 (1982) 247-256.

Thermal Destruction of Vitamin B_6 Vitamers in Buffer Solution and Cauliflower Puree. S. Navankasattusas, D.B. Lund. J. Food Sci. *47*, 1512-1518.

Thermal degradation rates of pyridoxal (PL-HCl), pyridoxine (PN-HCl) and pyridoxamine (PM-2 HCl) in 0.1 *M* phosphate buffer (pH 7.20) were determined over the temperature range 110–145°C using HPLC procedures. Thermal degradation of PM-2 HCl was modelled by a pseudo-first order rate constant. Thermal degradation of PN-HCl and PL-HCl was modelled by a 1.5 order and second order model, respectively. The temperature dependence of all three rate constants could be described by the Arrhenius equation. None of the degradation products from any of the vitamers exhibited antivitamin activity. Thermal degradation rates of vitamin B_6 in cauliflower puree were measured over the temperature range 106–138°C and found not to be described by a first-order model. The activation energy was markedly lower in this food system than in the model system and emphasizes the importance of conducting experiments on real food systems. The activation energy is in the range reported for several other water soluble nutrients.

Application of Leaching Model to Describe Potato Nutrient Losses in Hot Water Blanching. M.F. Kozempel, J.F. Sullivan, E.S. Della Monica, M.J. Egoville, E.A. Talley, W.J. Jones, J.C. Craig, Jr. J. Food Sci. *47*, 1519-1523.

Nutritive losses of hot water blanched potatoes were studied. The potatoes lost significant amounts of some amino acids—glutamic acid, aspartic acid, valine, phenylalanine, arginine, methionine and tryptophan. They also lost a significant amount of gamma-amino butyric acid. The concentration of the water soluble vitamins, ascorbic acid, riboflavin, thiamin, and niacin was significantly reduced. A leaching model, with diffusion as the rate controlling step, successfully predicted losses of these vitamins as a function of process parameters.

Variation of Vitamin Concentration and Retention in Canned Snap Beans from Three Processing Plants During Two Years. J.P. Van Buren, C.Y. Lee, L.M. Massey, Jr. J. Food Sci. *47*, 1545-1548.

A statistical evaluation of vitamin status during canning was obtained from samplings of raw, blanched and canned snap beans. With the exception of folic acid retention, it was not possible to distinguish the separate plants. This leads to the expectation that the season averages of vitamins from processing plants obtaining material from the same area would be similar. Retention percentages were lower for thiamin, folic acid and B_6 than for ascorbic, which was lower than for carotene. Raw material was a source of variation. Average concentrations in drained canned beans, dry weight basis were: ascorbic acid, 116 mg/100g; carotene, 22μg/g; thiamin, 3.4 μg/g; B_6, 5.3 μg/g; and folic acid, 7.3 μg/g.

A Computer Assisted Analysis of Some Theoretical Rate Effects in Mastication and in Deformation Testing of Foods. M. Peleg, M.D. Normand. J. Food Sci. *47*, 1572-1578.

Simplified rheological models, with relaxation times comparable to those of solid foods, were used to simulate stress strain relationships at rates comparable to those

in mastication and in common deformation tests (linear velocities on the order of 100 and 1 cm min^{-1} respectively). The simulations included the regimes of constant deformation and strain rates and a sinusoidal deformation pattern. They demonstrated that the information in sensory perception and mechanical testing can be different in both kind and magnitude largely due to the rheological character of the food and its relaxation time and to a lesser extent, to the exact deformation regime.

Analysis of a Model for Water Sorption Phenomena in Foods. C. Ferro Fontan, J. Chirife, E. Sanchio, H.A. Iglesias. J. Food Sci. *47*, 1590-1594.

The validity of the physical model on which the Hailwood and Horrobin (Trans. Fat. Soc 42B: 84; 1946) isotherm equation was developed was investigated. The results indicate that although the equation may fit sorption data for almost any type of food, it satisfies thermodynamic requirements (i.e. prediction of the temperature dependence) only for proteins and starchy foods. The results also show that plotting enthalpic changes against entropic changes for water sorption satisfies the enthalpy/entropy compensation phenomenon.

Heat Penetration for Sliced Mushrooms in Brine Process in Still and Agitating Retorts with Comparisons to Spore Count Reduction. M.R. Berry, Jr., J.G. Bradshaw. J. Food Sci. *47*, 1698-1704.

Retail and institutional cans of sliced mushrooms in brine were heated in still and agitating retorts. The F_0 values and heat penetration factors were determined from time-temperature data for various brine headspaces, reel speeds, and fill weights. Mushroom fill weight was the more critical parameter for simulated Sterilmatic and still processes. In the Sterilmatic, increasing the fill weight by 17 reduced the F_0 from 9.5 to 5.7 min. Compacting mushrooms during filling reduced the F_0 from 21.8 to 4.3 min in the still retort. A microbial method of process determination was conducted for selected agitated processes to compare with heat penetration. The integratd sterilization value, based on spore count reduction, exceeded F_0 by as much as 7.2 min in the 603 × 700 can, indicating the two sterilization values are not directly compatable.

Preconcentration of Apple Juice by Reverse Osmosis. M.J. Shfu, R.C. Wiley. J. Food Sci. *48*, 422-429.

Single strength apple juices (10° Brix) were processed by reverse osmosis to 20–25° Brix, primarily at 20°C. A pilot scale plate and frame UI-RO system, equipped with cellulose acetate (CA) membranes CA-865 and/or CA-990, or high resistance (HR) membranes, HR-95 and/or HR-98, was operated at pressures of 35–45 bar. At 45 bar, the larger pore-sized CA-865 possessed the highest processing capacity of 26.9 $L/m^2/hr$ (from 10° Brix to 20° Brix) and concentration limits of 35° Brix, but had low recovery of solates and flavor volatiles. The HR-95 and HR-98 had similar processing capacities of 15–16 $L/m^2/hr$ and concentration limits of 20–25° Brix at 45 bar. The recoveries of 97% solutes and 87% apple flavor volatiles were obtained using either the HR-95 or the HR-98.

Water Velocity Effect on Heat Penetration Parameters During Institutional Size Retort Pouch Processing. W.R.. Peterson, J.P. Adams. J. Food Sci. *48*, 457-459 & 464.

Institutional size retort pouches (15 × 12 × 1″) filled with 10% bentonite were processed in water with overriding air pressure. The heat penetration parameter, f_h, was measured at seven flow rates from 10 gal/min (Re=3000) to 110 gal/min (Re=33000). Apparent convection heat transfer coefficients (h-values) were calculated. Significant differences were found for both the h-value and observed f_h value as a function of flow rate. The h-values ranged from 33-48 BTU/hr ft^2 F and the observed f_h values ranged from 23.0–20.1 min for 10 and 110 gal/min. respectively.

Kinetics of Protein Quality Loss in Enriched Pasta Stored in a Sine Wave Temperature Condition. J.Y. Chen, K. Bohnsack, T.P. Labuza. J. Food Sci. *48*, 460-464.

The rate of loss of protein quality in enriched pasta was studied at constant temperature (30, 37 and 45°C) and under a continuous sine wave temperature fluctuation (25/45°C with a 24-hr period). Both loss of lysine by the fluoro-dinitro benzene (FDNB) method and a bioassay (*Tetrahymena thermophila* growth) for protein quality were employed. Significant loss of protein quality occurs in about 1 yr at temperatures above 30°C. The bioassay method showed that nutrient losses other than lysine could be occurring. Data from the constant temperature studies were used to predict the losses that occurred for the sine wave condition using the Hicks-Schwimmer model as modified with an Arrhenius approach. The prediction model gave about 15% error in comparison to actual losses. In addition, the rate of loss for the sine wave (25–45°C) was greater as predicted than the rate of loss at a constant mean temperature of 35°C.

Kinetics of the Maillard Reaction between Aspartame and Glucose in Solution at High Temperatures. J.A. Stamp, T.P. Labuza. J. Food Sci. *48*, 543-544 & 547.

Comparison was made of the extent of browning during accelerated storage tests of glucose/aspartame and glucose glycine model systems under steady state conditions of 70, 80, 90 and 100°C and an a_w of 0.80. Browning of aspartame followed zero order kinetics with a time of 0.1 absorbance units at 420 nm of 11.40, 5.3, 2.15 and 1.0 hr for each respective temperature. The activation energy (E_A) was 22.0 Kcal mole for the glucose/aspartame system and 15.5 Kcal/mole for the glucose/glycine system. The temperature sensitivities (Q_{10}) for the model systems were 2.4 and 1.9, respectively. The predicted shelf life to reach 0.1 absorbance units in an aqueous system at 45°C is 62 days compared to the actual value of 60 days.

Influence of Temperature on the Measurement of Water Activity of Food and Salt Systems. V.N. Scott, D.T. Bernard. J. Food Sci. *48*, 552-554.

The water activity of four salt slurries (barium chloride, potassium bromide, cobalt chloride and sodium bromide) and four foods (cheese spread, fruit preserves,

chocolate frosting and fudge sauce) was determined 10 times at approximately 20°C, 25°C and 30°C using an electric hygrometer. In general an increase in temperature resulted in a decrease in water activity. The magnitude of the decrease was typically greater between 25°C and 30°C than between 20°C and 25°C. This decrease was also greater when the substrate under test was in the lower a_w range. Thus temperature control is very important in inter-laboratory comparisons and when measuring water activity levels near critical values.

Freezing Time Prediction for Slab Shape Foodstuffs by an Improved Analytical Method. Y.C. Hung, D.R. Thompson. J. Food Sci. *48*, 555-560.

An improved analytical method for predicting the freezing time with one-dimensional heat transfer for slabs was developed. Tylose-MH-1000 was used as a model test material. The new model is similar to Plank's equation, but has a more theoretical basis. Total enthalpy difference instead of latent heat and weighted average temperature difference instead of the temperature difference between initial freezing point and freezer temperature were used in the improved prediction method. Linear regression was used to estimate shape parameters. Four different foods were used to test the model. Predicted times for foods were within 6% of the measured times.

A Diffusion Model with Concentration Dependent Diffusion Coefficient for Describing Water Movement in Legumes During Soaking. K.H. Hsu. J. Food Sci. *48*, 618-622 & 645.

A mathematical model based on Fick's diffusion equation with a concentration-dependent diffusion coefficient was proposed to describe the absorption of water by legumes. The equation was solved by using numerical scheme. Parameter study was performed. The model is capable of predicting sigmoidal-shaped water uptake curves common to many legumes. Differences are discussed between the surface resistance boundary condition used in this study and the radiation boundary condition widely used for dehydration calculations. The validity of using the proposed model to describe the water uptake of legumes was verified by the good fit between the experimental and theoretical curves.

Raoult's Law, Water Activity and Moisture Availability in Solutions. M. Caurie. J. Food Sci. *48*, 648-649.

A rationalization of Raoult's law has led to the conclusion that water activity (a_w) is a joint solution property of vapor pressure, solute and solvent concentrations. It is shown from this that a_w is not a measure of the absolute value of the mole fraction of water as indicated by Raoult's law but a measure of only a fraction of the mole fraction of water remaining free in solution available and unbound to solute molecules. The law is shown to overestimate this water activity (a_w) at all dilutions by an amount equal to the product of the mole fraction of solute and the lowered relative vapor pressure the solute generates in solution.

An Improved Model for Food Thickness from NonNewtonian Fluid Mechanics in the Mouth.. A.M. Dickie, J.L. Kokini. J. Food Sci. *48*, 57-61 & 65.

An improved model for food thickness has been developed which accounts for the transient viscoelastic behavior of food materials. This model, previously tested for spreadability, satisfactorily predicts subjective thickness as well. Subjective scores obtained through the use of ratio scales correlated well with calculated shear stress on the surface of the tongue. The best slope of thickness vs. shear stress on the tongue was 0.74 with a correlation coefficient of 0.93. The final result provides a desiign equation for the thickness of foods from a rheological standpoint.

Temperature Response of Frozen Peas to Di-Thermal Storage Regimes. S.K. Sastry, A. Kilara. J. Food Sci. *48*, 77-83.

A mathematical model was developed for prediction of temperature fluctuations in warehouse stacks of frozen peas subjected to dithermal storage regimes. The model was tested by comparing its predictions with temperatures measured in frozen peas packed into a slab-shaped container. Satisfactory agreement was found between model and experiment. Other model predictions indicate that large container sizes and rapid fluctuation regimes result in the greatest thermal stability at interior locations in bulk-stored peas. Thermal properties of frozen peas were also determined as part of the experimental verification. The model can be used to evaluate quality changes in frozen products due to di-thermal storage and the energy needed to maintain a certain final quality.

Gas-Particle Heat Transfer Coefficient for the Fluidization of Different Shaped Foods. A. Vazquez, A. Calvelo. J. Food Sci. *48*, 114-118.

Gas-particle heat transfer coefficients for the fluidization of diced potatoes and potato strips were measured in a batch fluidized bed in which wet particles were dried under constant rate period conditions. Thus, the surface temperature of particles was equal to the wet-bulb temperature of the air. The minimum fluidization voidage and velocity were also measured as well as the bed expansion characteristics. Results are expressed through Colburn's factor, as a function of a modified Reynolds number and an Archimedes number, allowing for the correlation of data for different shaped foods (potato cubes and strips, peas, etc.) into a single equation.

Moisture Sorpton Isotherms for Bacon Slices. R.P. Konstance, J.C. Craig, Jr., C.C. Panzer. J. Food Sci. *48*, 127-130..

There is substantial evidence that controlled dehydration of bacon products to a water activity of 0.92 or below should allow control of spore outgrowth and toxin production by *Clostridium botulinum* and permit reduction of added nitrate levels. This study presents sorption data necessary for the development of a practical dehydration technique for bacon. Variations in fat/lean ratio, storage temperature, sorption mode, and drying method result in changes to the moisture sorption isotherms. Of these parameters only fat/lean variability of bacon significantly

affects the isotherms at water activity levels above 0.90. Empirical equations for the isotherms were derived and used to establish differences in the isotherms due to variation in the parameters studied.

Moisture Loss in Tray Packed Fresh Fish During Eight Days Storage at 2 C. S.K. Williams, R. Martin, W.L. Brown, J.N. Bacus. J. Food Sci. *48*, 168-171.

Effects of moisture loss in tray-packed fresh fillets of Flounder (*pogonias cromis*), Red Snapper (*Litjanus blackfordii*), Croaker (*Micropogon undalatus*) and Ocean Perch (*Sebastes marinus*) were studied. The fish, purchased from seafood suppliers and processed into fillets at their prospective plants, were packaged in plastic foam trays lined with absorbent pads, overwrapped, and subsequently stored at 2°C (35.6°F) for 8 days. Gross and net weights decreased whereas the percent drip increased for all fish during storage. Except for croaker, the total moisture content remained virtually unchanged for all fillets during storage. The acceptability of all fillets decreased as the Trimethylamine-Nitrogen concentrations increased.

Storage Stability of Intermediate Moisture Mullet Roe. H.W. Hsu, J.C. Deng, J.A. Koburger, J.A. Cornell. J. Food Sci. *48*, 172-175.

A storage stability study was performed on intermediate moisture roe (a_w = 0.84, salt content = 4%). Samples were stored at various temperatures for up to 1 month. Microbial analyses indicated that bacteria could grow from 5–25°C. Fungi grew at 15° and 25°C while their growth was inhibited at 5°C; however, a lag phase was detected at 15°C. TBA values increased linearly during storage. Microbial analyses, chemical determination of rancidity and sensory evaluations showed that the product was still acceptable after 30 days storage at 5°, 15° or 25°C.

Vitamin C Retention of Potato Fries Blanched in Water. W.E. Artz, C.A. Pettibone, J. Augustin, B.G. Swanson. J. Food Sci. *48*, 272-273.

Vitamin C retention was determined microfluorometrically for French fries heated in water. Vitamin C retention for 1.3 cm (½ in.) water blanched French fries ranged from 83.2-54.1%. The French fry blanch times were 5, 10 and 15 min at 66°C, 77°C and 88°C. The apparent Ea was 4.0 kcal/mole.

Forced Air Drying of Partially Freeze-Dried Compressed Carrot Bars. E.R. Burns, L.J. Talley. J. Food Sci. *48*, 193-196.

The quality of compressed carrot bars produced by combining freeze drying with air drying was investigated. Quality parameters measured were color, texture, rehydration ratio, carotene, ascorbic acid, alphatocopherol, and sensory acceptance. It was found that a high quality compressed carrot bar could be obtained by freeze drying to 20–40% moisture, equilibrating with microwave energy, compressing, then air drying at 60°C. The scanning electron microscope proved useful in delineating reasons for differences in texture and rehydration.

Influence of Selected Thermal Processing Conditions on Steam Consumption and on Mass Average Sterilizing Values. S.R. Bhowmik, K. Hayakawa. J. Food Sci. *48*, 212-216 & 225.

The influence of can size, type of food (conductive or convective), retort temperatures, initial temperature of food and target sterilizing value on steam consumption was studied. A 2^5 factorial design of experiments was used. Steam consumption was measured by using steam flow meters. A mass average sterilizing value was computed for each process by using experimentally determined heat penetration parameters. Steam consumption was significantly high for processing larger cans compared to smaller cans both containing equal quantities of conduction heating food simulant. The can size had no significant influence on steam consumptions with the convection heating food simulant. Steam consumption and mass average sterilizing values were reduced significantly by employing a high retort temperature to obtain a high target F_p value. With a low target F_p value, the type of food simulant did not affect significantly mass average sterilizing value.

Heat and Mass Transfer During the Warm Water Blanching of Potatoes. A.N. Califano, A. Calvelo. J. Food Sci. *48*, 220-225.

A model of heat and mass transfer with simultaneous chemical reaction is proposed for analyzing the influence of operating variables on the reducing sugar content at the surface of blanched potatoes. This content is partially responsible for the color of the finished product. The involved parameters (potato thermal conductivity, heat transfer coefficient of the system and kinetic constants for overall reaction of reducing sugar generation) were evaluated in separate experiments. The apparent diffusion coefficient of reducing sugars in potatoes was the only parameter obtained from blanching experiments. Temperature and concentration profiles and effect of blanching temperature on surface reducing sugar content are analyzed using the developed model. The possible underestimation of the diffusion coefficient when simultaneous starch hydrolysis is not taken into account is also considered.

A Solid State Fermentation System for Production of Ethanol From Apple Pomace. Y.D. Hang, C.Y. Lee, E.E. Woodams. J. Food Sci. *47*, 1851-1852.

A sold state fermentation system for the production of ethanol from apple pomace with a Montrachet strain of *Saccharomyces cerevisiae* is described. The yields of ethanol varied from about 29 g to more than 40 g per kg of apple pomace, depending on the samples fermented. Separation of up to 99% of the ethanol from spent apple pomace was achieved with a rotary vacuum evaporator. The results of this study indicate that the alcoholic fermentation of apple pomace might be an efficient method of alleviating waste disposal problems with the concomitant production of ethanol.

Concentration of Tomato Products: Analysis of Energy Savings Process Alternatives. M.C. Dale, M.R. Okos, P. Nelson. J. Food Sci. *47*, 1853-1858.

Four process alternatives to the standard steam driven triple effect scraped surface evaporators are compared on a present value economic basis. Use of mechanical

vapor recompression (MVR) evaporators, reverse osmosis (RO), and centrifugal separation of tomato fiber and serum are compared in different combinations. The lowest cost system was found to utilize centrifugation, RO, MVR and heat recovery with a total energy use of 88.7 Kcal/kg (160 Btu/lb) of tomato concentrate as compared to the conventional system requiring over 1110 Kcal/kg (2000 Btu/lb) concentrate. The viscosity of the recombined solids-serum concentrate after a heat treatment was found to be 80% of the conventional concentrate. Mathematical models of the unit operations are developed and coupled with capital costs and energy costs for the unit operations to give present value system costs.

Energy Evaluation of an Ultra-High Temperature Shell and Tube Processing System. R.B. Biziak, K.R. Swartzel, V.A. Jones. J. Food Sci. *47*, 1875-1878.

Energy loads for a shell-and-tube ultra-high temperature (UHT) processing system were examined during start-up, equipment sterilization and product processing. Product flow rates were 606, 1022, and 1325 L/hr. Process temperatures were 138, 143, and 149°C. The regeneration section contributed from 57.5–70.4% useable heat. Energy use remained relatively constant for varying start-up conditions and increased as a function of flow rate during equipment sterilization. Energy inputs for product processing varied from 358-437 kJ/kg. Minimum energy loads occurred between flow rates of 1000 and 1250 L/hr. Longer processing times decreased the effect of equipment start-up and sterilization on overall process energy requirements.

Arrhenius Kinetics as Applied to Product Constituent Losses in Ultra High Temperature Processing. K.R. Swartzel. J. Food Sci. *47*, 1886-1871.

Product constituent losses in ultra high temperature processing were examined with Arrhenius kinetics. An iteration procedure was utilized to develop time-temperature relationships for tubular heating systems. After introduction of the time-temperature relationship onto the Arrhenius equation integration was performed to yield relationships representing product constituent losses. Time-temperature conditions for a direct system required to achieve the same losses were determined. A unique condition developed where direct and indirect systems may be designed having equivalent losses, independent of activation energies. An example is demonstrated utilizing whole milk heated by commercially available direct and indirect systems. Losses in five constituents were investigated for fifteen different indirect heating conditions. The mathematical uniqueness of the equivalence is examined.

Chlorophyll Degradation in a Spinach System at Low and Intermediate Water Activities. F.M. Lajolo, U.M. Lanfer Marquez. J. Food Sci. *47*, 1995-1998 & 2003.

Chlorophyll degradation in blanched freeze-dried spinach puree was studied in model systems as a function of water activity (a_w), pH, temperature and also in the presence of glycerol, a water-binding agent. For $a_w > 0.32$ the most important

mechanism of chlorophyll degradation is the transformation into pheophytin. The reaction can occur at very limited water concentration and has a first order dependence on pH, water activity and pigment concentration. The addition of glycerol increases the rate of degradation of chlorophyll. At temperatures higher than 56.7°C and $a_w \leq 0.11$, the energy of activation increased, indicating different mechanisms. For temperatures below 38°C the rate tended to increase instead of decreasing with decreasing temperatures because of changes in the sorption isotherm (increase of water content) caused by the shift in the temperature.

Mass Flow and Energy Use During Orange Peel Oil Recovery. R.J. Braddock, W.M. Miller. J. Food Sci. *47*, 2008-2010.

Electrical energy consumption and oil recovery were measured during operation of a commercial citrus peel oil centrifugation process. Two parts of a centrifuge's electrical consumption were identified: regular operation and the discharge cycle. During discharge cycles, the electrical energy ranged from 125–189% of the steady-state values. Energy costs were computed for the desludger and polisher centrifuges. Direct electrical costs for the oil mill totaled 0.67¢/kg oil recovered. Electrical costs calculated for finishing and dewaxing totaled 0.5¢/kg oil. Actual oil yield (1.1 kg/t) was only 20% of the total in the fruit. A major source of oil loss occurred during extraction from the fruit, where less than 50% of the oil was actually extracted into the dilute emulsion. Inefficient operation of the centrifuges accounted for most of the remaining losses.

Simplified Equations for Transient Temperatures in Conductive Foods with Convective Heat Transfer at the Surface. H.S. Ramaswamy, K.V. Lo, M.A. Tung. J. Food Sci. *47*, 2042-2047.

Simple equations were developed to predict the values of some characteristic transcendental and Bessel functions, and hence the temperature history in regular solid foods of finite and infinite dimensions under unsteady state conduction with convective heat transfer at the surface. For various combinations of Biot (0.02–200) and Fourier (>0.2) numbers, the mean error involved in predicting the unsteady temperature ratio using the developed equations was less than 0.1% as compared to the original models. Equations were presented for temperature at any location as well as the mass average temperature. The characteristic functions were related to the f and j parameters from heating and cooling curves.

A Simple Atmosphere Generating System for Experimental Storage of Fruits and Vegetables. O. Kane, M. Boulet, F. Castaigne, P. Marcellin. J. Food Sci. *47*, 2097-2098.

A simple system was developed for generating atmospheres of controlled relative humidities applicable to the experimental storage of fruits or vegetables. It is based on the mixing of two air streams in adequate proportions, one consisting of dry air and the other being air saturated with water vapors. Stable air flows and relative humidities were obtained in a storage experiment of 21 days duration.

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Page two should contain an abstract of not more than 150 words. This abstract should be intelligible by itself.

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