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ESTIMATION OF ARRHENIUS MODEL PARAMETERS USING THREE LEAST SQUARES METHODS

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ABSTRACT

The effectiveness of three least squares regression methods has been assessed for the estimation of Arrhenius model parameters. The performance of each method was assessed by comparing the relative sizes and positions of the 90% confidence regions for the parameter estimates and the degradation predictions. The traditional regression scheme, Method I, of sequentially regressing concentration data to obtain rates followed by a regression of the rates versus temperature to obtain the Arrhenius parameters was shown to be the least desirable method. Method II was similar to Method I, but used a multiple linear regression to regress the concentration data through a single c_o value. This provided more precise estimates, but a bias was indicated due to the fact that the individual rate estimates were not independent. Method III utilized a nonlinear regression which did not evaluate the individual rates. This method was less precise than Method II, but showed no bias. Method III was superior to Method I in every respect.

INTRODUCTION

The accurate prediction of a food product's stability is dependent on the development of an accurate kinetic model. Prediction errors can occur because the model is not of the correct functional form, because factors not considered by the model influence the food's stability, or merely because the model parameters are not accurately estimated. If either of

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the first two reasons cause the model failure, increased accuracy may require an extensive laboratory program to develop a new kinetic theory. However, if the model is inaccurate due to inaccurate parameter estimates, this might be remedied by reanalyzing the data in a more efficient manner.

For long term stability predictions, it is convenient to accelerate the tests by testing the product at elevated temperatures, and then extrapolate the test results to the milder conditions normally experienced by the product, knowing its temperature sensitivity (extrapolations far beyond the test region are not advisable both for statistical reasons and due to possible chemical shifts in the dominating step of a reaction mechanism). Even though there is an acceleration in the tests due to increased temperature, the tests often last many days, and require somewhat sophisticated, controlled environmental equipment. Consequently, relatively little data is collected, and it becomes essential to analyze the limited data in a way which tends to maximize confidence in predictions.

The Arrhenius equation,

$$k = k_o \exp(-E/RT) \tag{1}$$

is often used as a theoretical basis for the development of a mathematical description of the temperature sensitivity of a product. In addition to the temperature sensitivity predictions, the activation energy, E, is used to derive certain implications about the reaction pathway. To assure accuracy and confidence in conclusions drawn from the model, both the data generation and the parameter estimation techniques must be considered. The effects of the experimental design on the parameter estimate accuracy have been reported previously (e.g., Benson 1960). In this paper, the effects of the estimation techniques are presented.

Much of the kinetic information has been analyzed by linearizing the system of equations and performing successive ordinary (linear) least squares fits of the data. With respect to the application of the Arrhenius equation to a first order reaction, this means first regressing log c versus time to obtain the rates, k, and then regressing log k versus 1/T to obtain the estimates for E and k_o. This is not necessarily the most efficient way to analyze the data (Lund 1983), primarily because unnecessary parameters are estimated. Least squares estimation is appealing due to its computational and theoretical simplicity. The effects of the data regression technique are presented for three least squares regression methods, varying in complexity, for their ability to accurately estimate the parameters of the Arrhenius model. This is not to imply that least squares techniques are the only methods for the analysis of temperature dependent kinetic data, but these may be easily implemented.

EXPERIMENTAL

Data Generation

The analysis is illustrated on a hypothetical data set. Simulation of the data assures that a certain set of assumptions are in effect, i.e., the error structure in the observations and the model forms (first-order decomposition following an Arrhenius dependence). This eliminates bias in the parameter estimates due to faulty assumptions, and illustrates the possible bias due to the estimation procedure itself.

An exact set of data was generated using the model:

$$c_m = c_o \exp(-k_o \exp(-E/RT)\, t) \tag{2}$$

where:

$c_o = 100$,
$k_o = 2.0 \times 10^{12}$ and
$E/R = 1.0 \times 10^4\,°K$

at times spaced by tens from 0 to 100, and at 20, 30, 40, and 45°C. The parameter values are chosen from no particular system, but are representative of many typical reactions in foods (e.g., Labuza and Kamman 1983; Lund 1983). A set of simulated experimental data was generated by scattering the exact data with random normally distributed proportional (percent) error. This error structure is common for chemical measurements, and is discussed in other papers (e.g., Nelson 1983; Davies and Hudson 1981; and Askelöf *et al.* 1976).

The simulated experimental observations, c, were created by randomly scattering the exact concentrations, c_m, with variance proportional to c_m using a gaussian random number generator ($c \sim N(c_m, (c_m e)^2)$). A high, but not unusual, experimental error of 8% ($e = 0.08$) was chosen to magnify the effects of the observation error. Also, to simulate a chemical assay procedure with a detection limit, any simulated observation beyond 90% degradation was deleted. The data set ($N = 37$) is shown in Fig. 1.

Regression Schemes

Three least squares regression schemes are considered for a data set which contains m temperature categories ($m = 4$ in this example), and n_i ($i = 1, ..., m$) observations within each category. Thus, a total of

$$N = \sum_{i=1}^{m} n_i$$

observations are in the data set. To meet the assumptions for which least

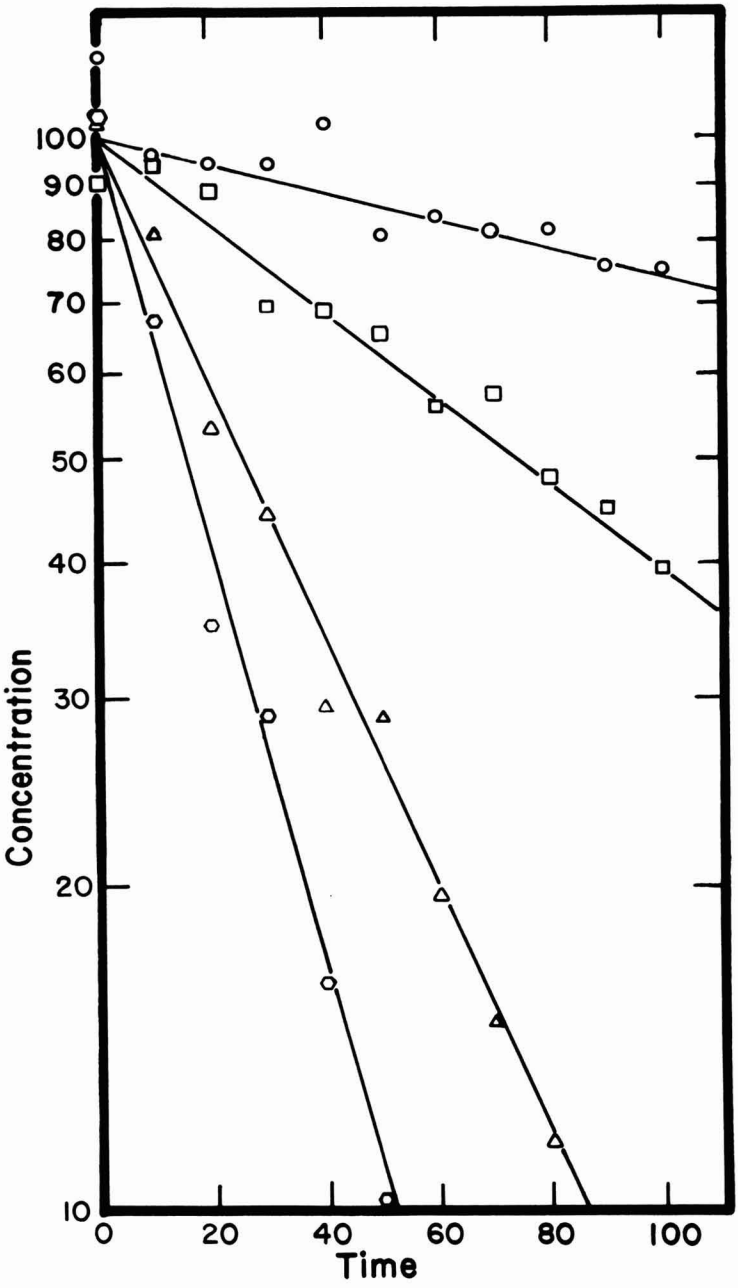

FIG. 1. DATA SET GENERATED FROM AN ARRHENIUS MODEL FOR TEMPERATURE OF 20°, 30°, 40° AND 45° (○, □, △, AND ⬡) THE CONCENTRATIONS CONTAIN AN 8% GAUSSIAN ERROR.

squares regression has been derived, it is necessary that the observations are independent and that the error is normally distributed with constant variance (homoscedastic). Observations with a constant percentage error are obviously not homoscedastic, but they may be transformed into a homoscedastic population by applying the variance stabilizing transformation log[concentration]. This is a particularly convenient transformation for first-order reactions, since it also linearizes Eq. 2 with respect to the reaction rate.

Method I: Separate Linear Regression

Probably the most common method of analyzing this type of data is to first group the data into m separate temperature categories, then regress log c versus t to estimate the rates, k_i, at each temperature, and finally regress log k_i versus $1/T_i$ to obtain the estimates of log k_o and $-E/R$. This is expressed in equation form as first regressing

$$\log c = \log c_o - k_i t \tag{3}$$

at each temperature, and then regressing

$$\log k_i = \log k_o - E/RT_i \tag{4}$$

(subscripts which indicate individual observations have been omitted). It can be seen that in this analysis a total of $2m + 2$ parameters are estimated, since a separate log c_o is estimated at each temperature.

Method II: Multiple Linear Regression

If the same starting material is used at each temperature level, then it is only necessary to estimate one log c_o. The regression can gain strength by estimating fewer parameters and by analyzing the data set as a whole. The multiple linear regression technique is similar to the separate linear regression, but regresses the data together through a single log c_o value. The parameters from the regression yield rate estimates at each temperature, which are then fit to the Arrhenius equation (Eq. 4) to obtain estimates of log k_o and $-E/R$. To accomplish the multiple linear regression, the times must be introduced as pseudo-dummy variables, t_i. In equation form, this means regressing the observations according to:

$$\log c = \log c_o - \sum_{i=1}^{m} k_i t_i \tag{5}$$

The dummy time variables are creating by associating the reaction times at a particular temperature, T_i, with a parameter, k_i, and setting the dummy times associated with the other temperature levels to zero. Therefore, there are m dummy time variables where at most one rate parameter has a nonzero time for any given observation.

Method II is best illustrated in a simple example. For a stability test run at three temperatures, T_1, T_2 and T_3, with concentration measurements taken at three times, t_1, t_2 and t_3, in addition to an initial concentration determination, c_o, the data set used for the multiple linear regression appears in Table 1. This structure may be expanded for any number of times or temperatures. This regression gives the rates, k_i, associated with temperatures T_i.

Table 1. Construction of a data set for the multiple linear regression of Method II

No.	Transformed observation	Dummy time variables		
		T_1	T_2	T_3
1	$\log c_0$	0	0	0
2	$\log c_1$	t_1	0	0
3	$\log c_2$	t_2	0	0
4	$\log c_3$	t_3	0	0
5	$\log c_4$	0	t_1	0
6	$\log c_5$	0	t_2	0
7	$\log c_6$	0	t_3	0
8	$\log c_7$	0	0	t_1
9	$\log c_8$	0	0	t_2
10	$\log c_9$	0	0	t_3

Regress the transformed observations versus the dummy time variables. The intercept will estimate $\log c_o$, and the slopes will estimate the rates $-k_1$, at T_1, $-k_2$ at T_2, etc.

This regression is most easily done on a computer. For this work, the statistical package TROLL was used. Many other packages exist which do this kind of analysis relatively efficiently, such as BMDP, SPSS, SAS or MINITAB. Some packages are even available for use on personal computers. TROLL was chosen because it solves a wide variety of types of regression problems and provides the appropriate statistics to construct confidence regions and provides a large number of regression diagnostics for the identification of bad, influential and collinear data (Belsley *et al.* 1980). For more information and documentation on TROLL, one may write Publications Office, Information Processing Services, MIT Room 11-313, Cambridge, MA 02139.

In the absence of a computer, the multiple linear regression can be accomplished on a hand calculator, or approximated graphically, using a technique of fitting by stages (Mosteller and Tukey 1977). This method has the disadvantage that it may become very lengthy as the number of temperature levels increases. Unlike most of the statistical packages for computers, this method does not provide any diagnostic statistics to aid in the regression.

Method III: Nonlinear Least Squares Regression

The nonlinear regression performs a single regression on all of the data to estimate log c_o, k_o, and E/R directly, without calculating the rates at each temperature. Equation 2 is not easily regressed directly, since the parameters are highly collinear (interdependent). This causes many of the numerical methods which are utilized in nonlinear regression packages to fail. A transformation of the equation improves this situation (Nelson 1983), and improves the rate of convergence of the curve fitting procedure. Equation 2 is transformed to:

$$\log c = \log c_o - \exp[A - E/R((1/T) - \lambda)]t \tag{6}$$

where:

$$A = \log k_o - \lambda E/R \tag{7}$$

$$\lambda = \frac{1}{m} \sum_{i=1}^{m} \frac{1}{T_i} \tag{8}$$

For this transformation, the variance of the parameter estimate, log k_o, may be expanded in terms of the other parameters

$$V(\log k_o) = V(A) + \lambda^2 V(E/R) + 2\lambda \mathrm{Cov}(A, E/R) \tag{9}$$

The covariance, or interdependence, of the parameters log k_o and E/R may be calculated from:

$$\text{Cov}(\log k_o, E/R) = \lambda V(E/R) + \text{Cov}(A, E/R) \tag{10}$$

or

$$r = \frac{\text{Cov}(\log k_o, E/R)}{\sqrt{V(\log k_o)\, V(E/R)}} \tag{11}$$

where r is the correlation coefficient between the parameters.

It is necessary to have access to a computer, and some regression software to be able to calculate the nonlinear regression parameters. TROLL was used for this purpose in this work.

RESULTS AND DISCUSSION

Two basic criteria are used in the evaluation of the regression schemes; the accuracy and precision of the parameter estimates, and the accuracy and precision of the predicted reaction rates. The parameter estimates are judged on the size of the joint confidence region for the estimates. The joint confidence region is the region in which the true parameters probably exist together at a specified confidence level. The extremes of the 90% joint confidence ellipse approximately correspond to the ends of the 95% confidence intervals for the individual parameters (the joint probability of two events at 95% probability is approximately 90%, i.e., $(0.95)^2 \approx 0.90$). Since the parameters are so highly correlated, the ellipse is a more accurate representation than the separate confidence intervals because a parameter pair may be well within the separate 95% confidence intervals, but may be very unlikely to occur since it is very far outside of the 90% joint confidence region. The region is constructed by considering both the variance and covariance of the parameter estimates, and by assuming the estimates are from a bivariate normal distribution. The accuracy of a rate prediction is estimated by locating the extreme predictions associated with the boundary of the confidence ellipse.

The confidence regions reported here which refer to a nonlinear regression are approximate. Generally, in nonlinear regression, the confidence region is some sort of deformed ellipse (i.e., the estimates are not distributed as a bivariate normal), but in the calculation done by TROLL, the region is approximated by a linear equation, and this is carried throughout the analysis.

Table 2. Rate estimates from Methods I and II

Method	temp. °C	n	log c_o	rate $k \times 10^3$	Standard Error		
					log c	$k \times 10^3$	log k
Actual	20	11	4.6052	3.011			
	30	11	4.6052	9.287			
	40	9	4.6052*	26.657			
	45	6	4.6052	44.053			
I	20	11	4.6700	3.689	0.0374	0.632	0.1713
	30	11	4.5820	8.646	0.0337	0.569	0.0658
	40	9	4.5992	27.028	0.0482	1.013	0.0375
	45	6	4.6226	45.698	0.0720	2.378	0.0520
II	20	11	4.6188	2.898	0.0220	0.485	0.1640
	30	11	4.6188	9.173	0.0220	0.485	0.0529
	40	9	4.6188	27.206	0.0220	0.639	0.0233
	45	6	4.6188	45.596	0.0220	1.146	0.0251

The rates estimated by Methods I and II are given in Table 2. To obtain estimates for the Arrhenius parameters, the usual procedure at this point is to do the linear regression log k versus 1/T to obtain estimates for log k_o and $-E/R$ (Eq. 4). As in all least squares regression, it is important to verify that the assumptions which motivate the least squares are met, and as mentioned previously, an important assumption is that the observations are homoscedastic. Thus, the transformed observation, log k, should have constant variance. The variance of a transformed observation, $Y = f(X)$, can be approximated from a Taylor series expansion, such that

$$V(Y) = \left|\frac{dY}{dX}\right|^2 V(X) + \text{higher order terms} \qquad (12)$$

The values for $\sqrt{V(\log k)}$ also appear in Table 2.

An F-test reveals that the log-transformed rates are not homoscedastic, but the rates themselves could be (at 95% confidence). These results are not overwhelmingly convincing, however. In support of this conclusion is the fact that for the multiple linear regression (Method II) with equally spaced and an equal number of observations at each temperature level, the standard errors are identical. Therefore, it does not seem to be appropriate to regress log k versus 1/T using least squares.

Table 3. Effect of the regression scheme on the Arrhenius parameter estimates

Method	log k_o	E/R	Standard Error log k_o	Standard Error E/R	r
actual	28.324	10,000			
I-OLS	26.645	9,472	1.865	571	.99950
I-NLS	29.568	10,384	1.171	371	.98575
II-OLS	29.023	10,212	0.163	50	.99950
II-NLS	29.101	10,236	0.162	51	.99994
III	29.207	10,269	0.936	296	.99981

NOTE: The Arrhenius parameters are calculated from the estimates of the reaction rates using either an ordinary (linear) least squares (OLS) regression or a nonlinear least squares (NLS) regression.

A nonlinear regression, which regresses k on T to estimate the Arrhenius parameters was done. Since the Arrhenius parameters are typically highly collinear, as in Method III, the Arrhenius equation was transformed similar to Eq. 6, giving:

$$k = \exp [A - E/R ((1/T) - \lambda)] \tag{13}$$

where Eq. 7 to 11 also apply. The effect of the regression scheme on the parameter estimates are given in Table 3.

Table 3 shows that the parameter estimation procedure has an effect on the estimates, both in accuracy and precision. The simplest estimation method, Method I, is the least accurate, most probably since it estimates many parameters. Once the rates are determined, the nonlinear estimation of the Arrhenius parameters is superior for Method I. There is not as clear an advantage for the nonlinear regression with Method II.

The ellipses from the two linear methods are shown in Fig. 2. It can be seen that the parameters from Method II are predicted with a great deal of confidence, but the confidence region does not include the true parameter values, indicating a bias (inaccuracy) in the estimate. The bias in Method II likely occurs because the rates are not independent (i.e., they are correlated through the multiple linear regression), thus violating a basic assumption of least squares regression. Even with the bias, however, Method II is more accurate than Method I.

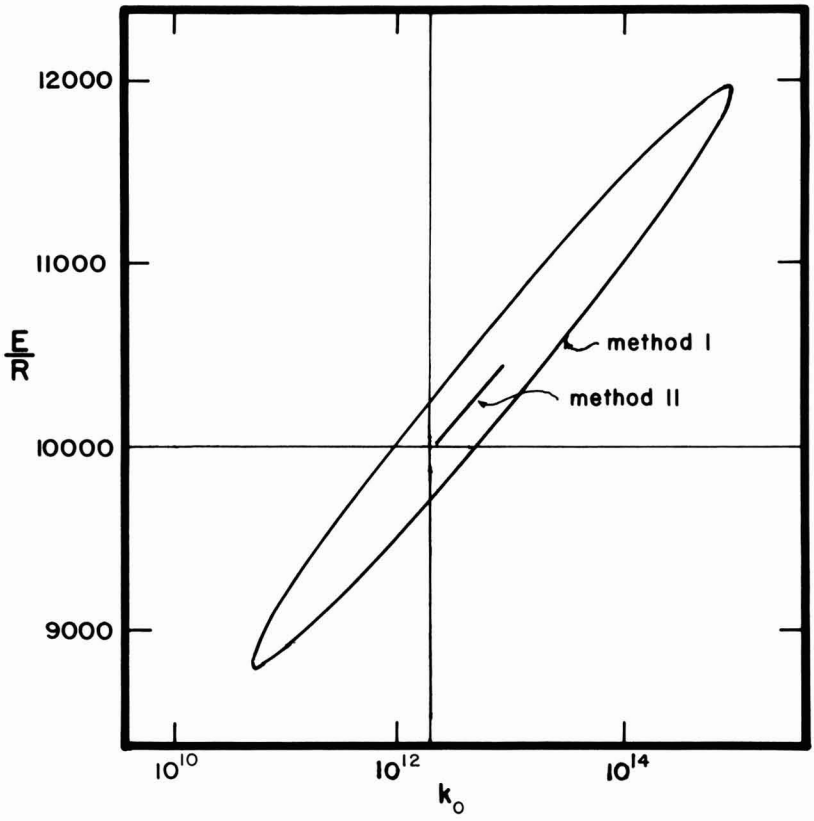

FIG. 2. THE 90% JOINT CONFIDENCE ELLIPSES FOR THE PARAMETERS k_0 AND E/R FROM METHODS I AND II

In comparing Method III with Method II (Fig. 3), Method III gives a larger confidence region (less precise), but apparently unbiased. This region is also significantly smaller than the region associated with Method I. The large confidence region may be due to the linear approximation of the shape of the region. The improvement in the estimates obtained via Method III over Method I is probably due to the fact that Method III gains strength through the analysis of the whole data set, and estimates fewer parameters.

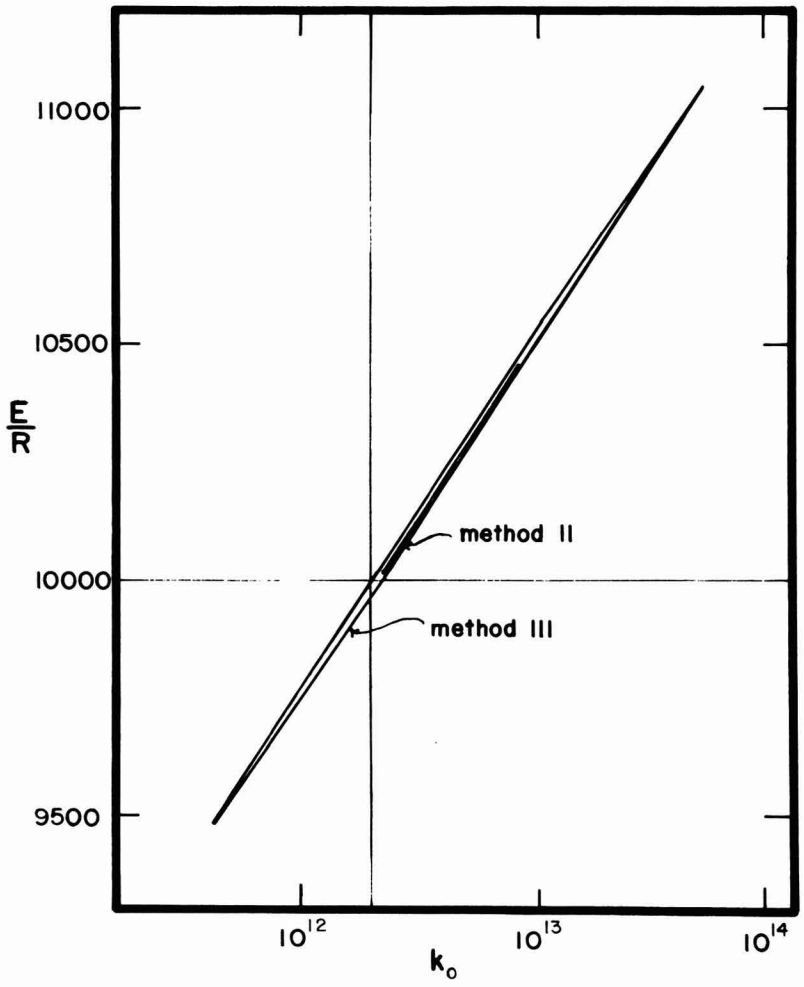

FIG. 3. THE 90% JOINT CONFIDENCE ELLIPSES FOR THE PARAMETERS k_o AND E/R FROM METHODS II AND III FOR METHOD III, THE ELLIPSE IS THE LINEAR APPROXIMATION OF THE TRUE 90% CONFIDENCE REGION FOR THE NONLINEAR REGRESSION.

The ellipses shown in Fig. 2 and 3 can also be used to demonstrate the effects of a parameter estimation scheme on the individual parameter E/R. The conclusions are the same as those drawn for the regions themselves, but it is useful to examine the magnitude of the effect.

Frequently, the models identified from the data are used for predictive purposes only. Therefore, it is important to relate the effects of the parameter estimation scheme on the possible predictions. For this, the

Table 4. Effect of regression scheme on predictions (90% confidence band)

Method	5°C			25°C		
	low	mid	high	low	mid	high
Rates ($k \times 10^3$)						
Actual		0.4774			5.338	
I	0.1337	0.4157	1.2923	2.029	5.099	12.813
II	0.4038	0.4445	0.4894	5.035	5.261	5.498
III	0.3123	0.4386	0.6158	4.470	5.233	6.124
Half-lives						
Actual		1452			130	
I	536	1667	5184	54	136	342
II	1416	1559	1717	126	132	138
III	1127	1580	2219	113	132	155

extreme rates and half-lives associated with the locus of parameters on the confidence ellipse are used to generate the extreme predictions. These values appear in Table 4 for two representative temperatures; 25°C which is within the data range, and 5°C which represents an extrapolation situation. These results essentially agree with the previous findings, that Method I is the least attractive, Method II is precise but biased, and Method III is quite good.

A similar analysis can be developed for pseudo-zero order reactions. For such systems, the linear equations to be regressed are of the form

$$c = c_o - kt \quad (0 < t < c_o/k) \tag{14}$$

For linear regressions to be unbiased in this situation it is required that the error in concentration measurement be a constant absolute error not percentage error, i.e., $c \sim N(c_m, e^2)$. If this error structure can be justified in an experimental setting, then methods may be applied which are similar to the three methods shown in this paper. Similar conclusions would be expected.

The discussion has surrounded observations made in the analysis of a single hypothetical data set. Extensive calculations must be carried out to obtain the true distributions of the parameter estimates. This can be accomplished by continuing this analysis on many other hypothetical data sets and using a Monte Carlo approach to develop the parameter distributions. The results would then be more quantitatively correct, but the qualitative conclusions are expected to be the same. Another area to

be examined is the possible use of weighted least squares techniques for Methods I and II. This would use the variances calculated for the rate estimates to weight the regression for the Arrhenius parameters.

CONCLUSIONS

The traditional analysis (Method I) gives the least accurate estimates for the Arrhenius parameters probably because it estimates too many intermediate values, and does not gain any strength in the regression by considering the data set as a whole.

The multiple linear regression (Method II) showed an improvement, but also showed a bias, which is likely due to the fact that in the final regression of k versus T, the rates are not independent, violating a basic assumption of least squares regression. The method, in the case demonstrated, gives very precise predictions of the rates, even though the parameter estimates are bias. Since the method is computationally less taxing than Method III, it could be 'good enough' for use in predictive models.

Method III is a very good method since it gives both an unbiased and precise estimation of the parameters. It is clearly the method of choice if the purpose of the analysis is to make statements concerning the activation energy of a reaction. Also, Method III is a more appropriate method theoretically, since it does not estimate unnecessary parameters, and does not need to be overly concerned about the theoretical implications of doing regressions on regression parameters. The method does, however, require more sophisticated computational techniques.

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A REVIEW OF TEXTURAL DEFECTS IN COOKED RECONSTITUTED LEGUMES – THE INFLUENCE OF STORAGE AND PROCESSING

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ABSTRACT

Legumes provide an important part of the world's protein requirements, as well as other nutrients, but they are underutilized as food. A major factor limiting expanded consumption is storage induced textural defects that prolong cooking time and demand correspondingly higher energy requirements for preparation. Estimates of losses due to hardening are difficult to obtain but show the economic importance of the problem. These defects, including the hard-to-cook phenomenon and hard shell, are initiated by structural and compositional factors but can be at least partially controlled by storage and processing conditions. The available literature on bean hardening is reviewed from which it may be concluded that adverse storage conditions (high temperatures and humidities) consistently produce these defects. A kinetic approach is taken to the hardening problem, including hydration and cooking, which should allow a better understanding of the processes involved. Methods that can be utilized to produce better cooking legumes are reviewed as are processing alternatives including disruption and dry fractionation, wet fractionation, extrusion, enzymes and animal feeding. The influence of hardening on the nutritive value of legumes, although not extensively studied, is examined and it is concluded that protein quality and the availability of essential amino acids can suffer. A course of action for future research is recommended.

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INTRODUCTION

Legume foods have been called "the meat of the poor", suggesting their important role in supplying much needed protein among lower socioeconomic groups. Different areas of the world show a marked preference for a few types of dried legumes as shown in Table 1 and it has been suggested that civilization foci evolved depending on them and nutritionally complementing staple cereals (Sauer 1969).

Recent population pressures on food availability have been addressed internationally by technological solutions aimed at increasing yields through a more intensive use of agricultural inputs such as irrigation, fertilizers, energy and improved varieties. Indeed, the impact of this "green revolution" on the world production of grains, particularly cereals, has been enormous (Jennings 1976). The overall effect in developing countries, however, is somewhat blurred by socio-economic problems and by the fact that this larger production enters the same antiquated food pipeline to reach the final consumer. In the case of legumes, increases in production are less spectacular than for cereals and they also face severe postharvest handling problems, the major ones being physical losses and the development of textural defects during storage including hard-to-cook and hard shell.

Table 1. Preferred legumes in different areas of the world

AREA	LEGUME
EUROPE	DRY BEANS (*PHASEOLUS VULGARIS*), DRY PEAS (*PISUM SATIVUM*), DRY BROAD BEANS (*VICIA FABA*)
NORTH AMERICA	DRY BEANS
LATIN AMERICA	DRY BEANS
NEAR EAST	DRY BROAD BEANS, LENTILS (*LENS CULINARIS*)
FAR EAST	DRY BEANS, CHICKPEAS (*CICER ARIETINUM*) PIGEON PEAS (*CAJANUS CAJAN*)
AFRICA	DRY BEANS, COWPEAS (*VIGNA UNGUICULATA*)

A companion article (Stanley and Aguilera 1985) addressed the influence of structure and composition on textural defects of cooked legumes. The present review emphasizes the much neglected storage and processing aspects as related to quality defects.

Postharvest Losses of Legumes

There have been few systematic efforts to determine postharvest losses of plant foods. In the case of grain crops they occur by a combination of three main factors acting in a cummulative manner: (1) predation by birds and rodents while the crop is being dried; (2) difficulty in achieving effective drying and prevention of moisture pickup which results in quality losses during storage, and (3) a massive problem of insect infestation (McDowell 1984). The enormous losses resulting from the action of these three vectors would provide more than the annual minimum caloric requirements of 168 million people (NAS 1978). Table 2 presents some

Table 2. Reported losses of selected legumes within the Postharvest System

Country	Total Weight Loss (Percent)	Reported National Production ('000 Tonnes)	Remarks
Ghana	7-45	11	Shelled beans, 1-5 months, unshelled beans, 22
Nigeria	5.4	932	Cowpeas
	1-2		Cowpeas stored 3 months in shell
	20[a]		Cowpeas
Kenya	30	280	On-farm storage
Zambia	40	600	Cowpeas
India	8.5	12,956	Pulses, central storage
Indonesia	5	900	Unspecified storage
Pakistan	5-10	785	Pulses
Belize	20-50	1	Kidney beans, on-farm storage
Brazil	15-25	1,923	Dry beans
Costa Rica	24		Dry beans
Honduras	20-50	48	Dry beans, on-farm storage
Nicaragua	10-35	54	Dry beans

Source: NAS (1978)
UNIDO (1979)

reported losses of legumes in the developing world, where 60-70% of the stock grain is kept in local storage by farmers or merchants (UNIDO 1979).

It is practical to separate postharvest losses of dry legumes due to textural defects from those caused by other factors. The former are more difficult to quantify and are rarely reported in the literature. In a recent survey conducted by INCAP in Guatemala, farmers indicated the loss due to seed hardening to be the most significant, affecting between 3.33 and 32.14% of the total production (INCAP 1983). Insect damage is the major cause of physical loss in pulses (Adams 1977). Harvested legumes usually carry a field infestation, mainly of bruchid beetle species, which lay their eggs on the maturing pods.

Governments have sustained large economic losses due to postharvest mishandling of beans. In Nicaragua, losses due mainly to insects, amounted to 5,240 tonnes in 1975, valued at about 2.4 million U.S. dollars (Giles 1977). In Central America and Panama, beans that developed the hard-to-cook condition during prolonged storage resulted in losses equivalent to 12 million U.S. dollars in 1977 (Gonzalez 1982). Another documented case occurred in Guatemala where 5,000 tonnes of beans purchased by the government at US$0.66/kg had to be sold at US$0.15/kg after inadequate handling and storage (Booth 1980).

Hardening During Storage: Analytical Data

There are several studies presenting quantitative data on the effect of storage on bean hardening. Three main aspects make analysis of this information difficult: (1) the fundamental parameters describing storage conditions, such as moisture content of the beans, temperature and relative humidity of the environment, are not adequately reported for the whole period; (2) the protocol for sample preparation and cooking varies in terms of the steps followed, level of the process parameters, age of the beans, instrumentation used, etc.; (3) textural deterioration of beans with time is evaluated by widely different methodologies ranging from "cooking times" at different pressures to "hardness", represented by the maximum force detected by instrumental means.

The data available, however, are consistent in demonstrating that hardening of beans under adverse storage conditions is a pervasive phenomenon. Figure 1 summarizes information reported in four studies for black beans stored at around 12% moisture and at 25°C. In order to make comparisons, relative hardness has been defined as either the maximum force or the cooking time at any time divided by the value at the beginning of the study. In spite of all the methodological differences discussed before, the data follow a trend that could be represented by a zero ($N = 0$)

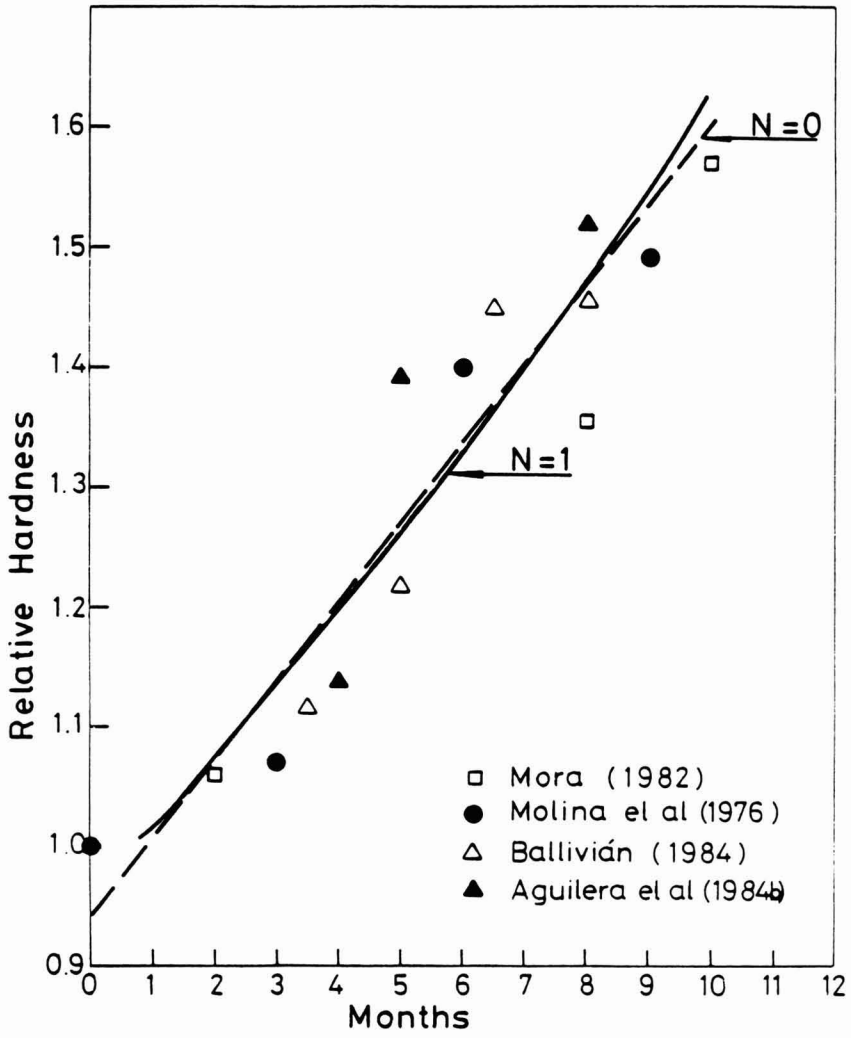

FIG. 1. RELATIVE HARDNESS (HARDNESS AT ANY TIME/HARDNESS AT TIME ZERO) OF BLACK BEANS STORED AROUND 12% MOISTURE AND 25°C
N Is The Reaction Of The Fitted Kinetics

or first (N = 1) order reaction. Thus, after 10 months of storage at these relatively mild conditions, beans would require a 60% longer cooking time to soften and approximately an equal amount of extra fuel. Under severe but nevertheless real storage conditions such as those in the tropics, hardening becomes uncontrollable. Antunes and Sgarbieri (1979) reported that beans with initial cooking times of 60 min could not be softened even after 300 min when stored for six months at 37°C and 76%

R.H. Similar results have been reported by Muneta (1964) and Luse (1982) among others.

High moisture content in beans greatly accelerates hardening, particularly when it is in excess of a certain critical value. The early work of Morris and Wood (1956) reported practically no change in flavor, lipid acidity and texture in beans stored for 2 years at 25°C and below 10% moisture. However, the rate of deterioration increased almost exponentially above a moisture level of 10-11%, corresponding to a water activity of 0.3 to 0.45 Acker (1969) and others have demonstrated that enzymatic activity (e.g., lipase) is restricted at a_w's below 0.3 and that at higher values it parallels the sorption isotherm. Figure 2 summarizes the relationship found between a typical moisture isotherm for beans and deterioration processes of enzymatic (lipid acidity), physical (texture) and microbiological activity. Much further research is needed to fully disclose

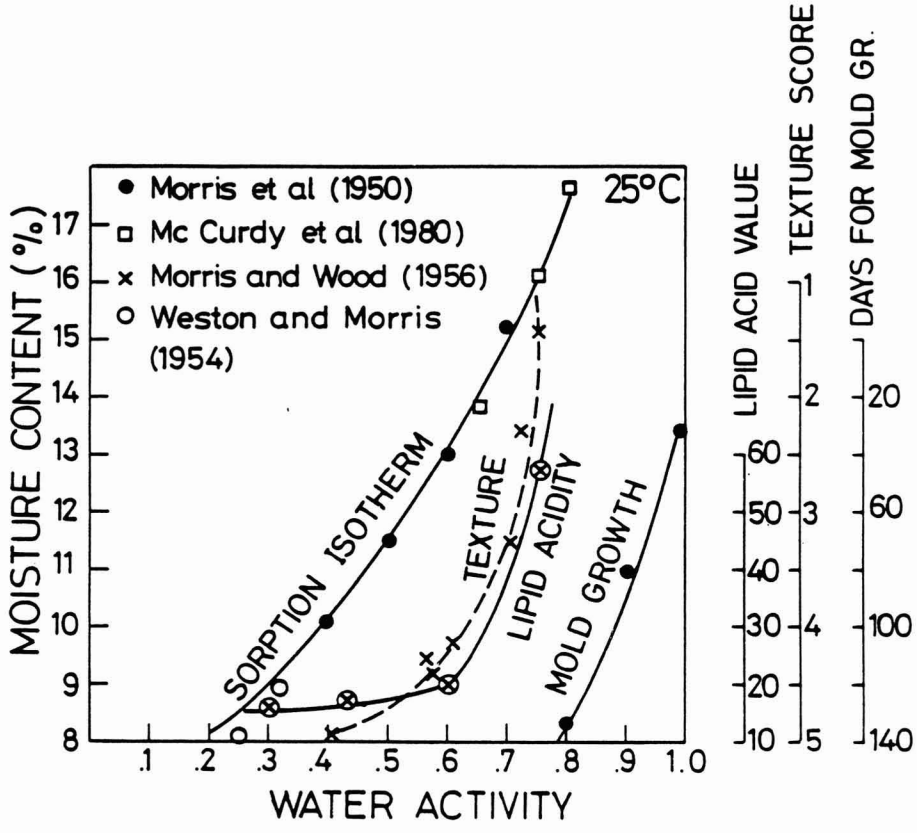

FIG. 2. REPRESENTATION OF THE SORPTION ISOTHERM AND STABILITY MAP FOR BEANS AFTER PROLONGED STORAGE

the relationships between the rates of deterioration and the sorption isotherm since dry beans are stored at reduced water activities. This should provide an insight into the relative importance of different mechanisms and a basis to predict losses during storage.

Several studies seem to agree that at refrigeration temperatures (0-5°C) minimal changes in hardness occur (Molina *et al.* 1976; Moscoso 1982). Storage in the range of 12-20°C also induces only minor alterations in texture (Burr *et al.* 1968; Luse 1982; Gonzalez 1982). For example, in the work of Antunes and Sgarbieri (1979) beans stored at 12°C and 52% R.H. showed practically no change in hardness during the first six months.

All information available indicates that impairment in the cooking quality of beans may be overcome by artificially dyring beans to a safe moisture level and subsequently preventing moisture pickup and/or by using refrigeration. In the case of tropical countries the first alternative is the only practical one worthwhile of being considered.

Hardening During Storage: A Kinetic Approach

From an engineering viewpoint the study of quality changes in beans during storage should be aimed at generating a model that predicts or simulates the phenomenon under various conditions. Modeling has been successfully used in food processing and storage (Lund 1983a; Karel 1983) and to predict physical changes (Lund 1983b). A preview of the potential of a kinetic model as applied to beans is illustrated using the data of Burr *et al.* (1968). These authors reported changes in cooking times of pinto and large lima beans at three temperatures (4, 12 and 21°C) and different moistures ranging from 8.9 to 16%. By assuming a zero order reaction model, a reaction rate constant (k) can be calculated from:

$$\frac{d\Theta}{dt} = k$$

where

Θ = cooking time at observed time (min)
t = storage time (months)
k = reaction rate constant

This model implies that the rate of loss in quality (longer cooking time) is constant with storage time and independent of the hardness of the bean at any time. A graph of storage time versus cooking time should be a straight line with slope equal to k. Figure 3, for lima beans, shows that k is a function of moisture content and temperature. Hence, changes in

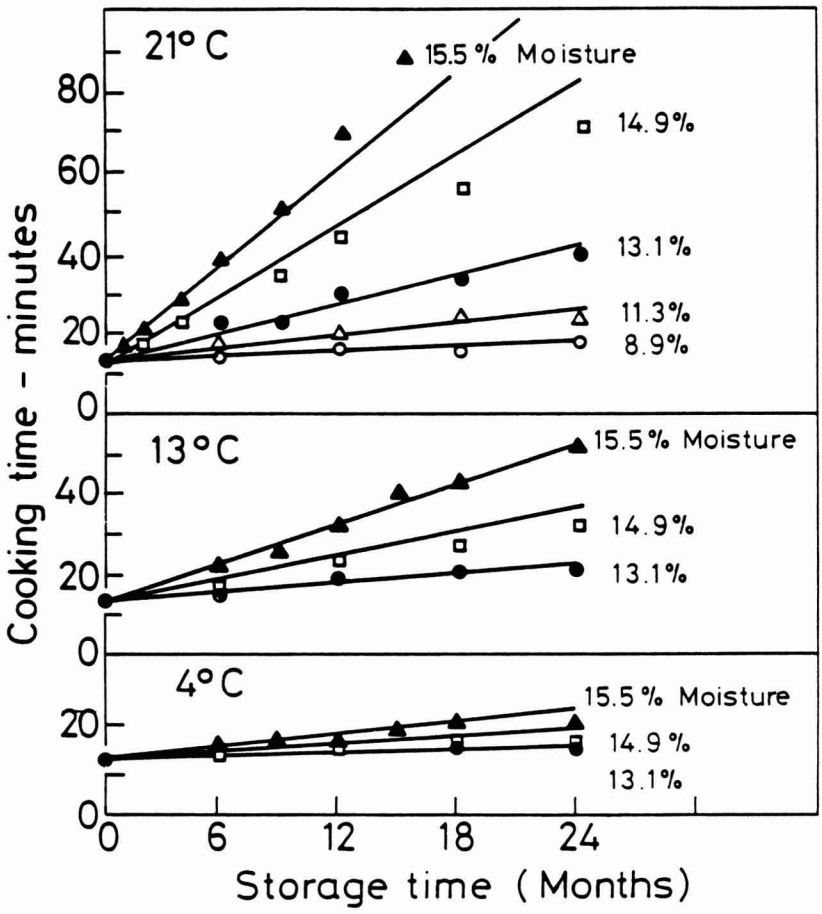

FIG. 3. ZERO ORDER KINETIC MODELING OF THE DATA OF BURR *ET AL.* (1968)
Solid Lines Represent The Values Predicted By The Model

cooking time may be more accurately predicted by a model such as:

$$\frac{d\Theta}{dt} = k_o (W)\, e^{(-E_a W/RT)}$$

where

k_o = a factor that depends on the moisture content
W = moisture content, %
E_a = energy of activation, kcal/mole
R = molar gas constant, 1.987 cal (°K mole)
T = absolute temperature, °K

The actual model describing the data of Burr *et al.* (1968) is:

$$\ln\left[\frac{(\Theta_f - \Theta_o)}{t}\right] = (0.5181\ W - 6.6391) + (1.0505\ W - 26.26)(1000/T - 3.401)$$

where Θ_o and Θ_f are the cooking times at the beginning and at any storage time t, respectively. Lines in Fig. 3 represent the cooking times as predicted by this model. Except for the cases of 14.9 and 15.5% moisture at 21°C all predicted values fall within 10% of the experimental data. The model is also accurate in simulating hardening for the first twelve months for all moisture contents and temperatures. A higher order relationship between E_a and W would provide for an even better fit. Important applications of this type of model are in accelerated storage tests and to predict cooking times under unsteady storage conditions (Labuza and Kamman 1983).

The energies of activation calculated from this model vary between 18.7 and 27.0 kcal/mole in the moisture range of 16.0 to 12.0%. Reactions involving losses in texture and flavor as well as those of enzymatic origin have E_a's in the range of 10-30 kcal/mole (Labuza 1972), which further supports the hypothesis of an enzymatic component in the hard-to-cook phenomena.

Kinetics of Hydration and Cooking

Preparation of legumes for eating involves hydration followed by cooking. The dramatic physical changes that occur can sometimes be adequately described by chemical kinetic models (Lund 1983b). A study by Loh and Breene (1982) showed a first-order model to be adequate in describing textural changes during heating.

Quast and da Silva (1977b) found that the semilogarithmic graphs of hydration time versus temperature for black beans were not straight lines, with z values varying between 40-200°C. Similar experiments performed by Kon (1979) with small white beans and Kubota (1979) with red beans resulted in sigmoid-shaped curves when a dimensionless soaking ratio was plotted against time. The apparent activation energies were in the order of 10 kcal/mole which confirmed that hydration by soaking is controlled by the diffusion process.

There seems to be some confusion regarding the kinetics of legume cooking. Quast and da Silva (1977a) and Silva *et al.* (1981) found that semilogarithmic plots of texture (force) versus cooking time for black beans were not straight lines as required by first order kinetics. Sefa-Dedeh *et al.* (1978) and Sefa-Dedeh and Stanley (1979) working with

cowpeas concluded that the rate of cooking for the time during which the middle lamella was visibly softening (up to 45 min at 100°C) followed first order kinetics. This holds true also for the former data during an initial period after which the cooking reaction tends to become order zero. The temperature dependence of the cooking rates for water-soaked black beans had activation energies between 31.3 and 35.5 kcal/mole. High activation energies and changes in reaction order with time are also characteristic of starch gelatinization (Lund 1984). Thus, it may be postulated that cooking of beans comprises at least two phases: an initial phase characterized by middle lamella breakdown and cell separation that follows first order kinetics and a second phase where the predominant phenomenon is gelatinization of the starch granules inside the cells. This is in agreement with findings of Hahn *et al.* (1977) who reported that cell separation in water soaked beans occurred at about 76°C which was also the onset of intracellular starch gelatinization as followed by loss of birefringence. When degree of gelatinization as determined by chemical methods is used as a measure of doneness, full gelatinization required 90 min at 100°C in the case of soaked rough rice (Bakshi and Singh 1980).

A more thorough study on the kinetics of bean cooking and the interrelation between physical and chemical parameters and organoleptic properties should be highly rewarding in terms of the understanding the mechanism of hardening and also calculation of the energy savings that could be derived.

Processes to Improve Storage Stability

The methods utilized to produce better cooking legumes and to control or overcome the development of textural defects seem to have as their bases either a reversal of the phytate-cation mechanism or the inactivation of enzymatic activity, phytase or otherwise (Stanley and Aguilera 1985). For convenience, these techniques will be mainly grouped according to the operations involved. Also included are several processes that produce undesirable effects.

Heat. The use of heat is a common method to inactivate enzymatic activity in foods. Molina *et al.* (1976) employed this approach in developing a process to reduce textural defects in stored black beans. When samples were treated by retorting or by heating under atmospheric steam, it was found that hardness was retarded during 9 months of storage at 25°C and 70% RH. As well, the heat treatment exerted a beneficial influence on water absorption capacity of the beans but this was not correlated to hardness. It is of importance to note that although moist heat treatments succeeded in reducing hardness relative to an unheated control, all the treatments hardened during storage when compared to a heated sample kept at 4°C. The more severe the heating

treatment, the more hardening occurred. Another most interesting finding in this study was that elevated storage conditions produced a noticeable increase in lignified protein that paralleled closely ($r = 0.91$) the development of hardening. Heat treatment slightly reduced lignification in the cotyledons but not in the seed coat, however, none of these values were close to the much lower results obtained for samples stored at 4°C. It should also be noted that the intensity of cotyledon color decreased as lignified protein increased, implicating polyphenols in this reaction. Thus, in highly colored beans, if enzymatic reactions, presumably phytase, are eliminated by heat a delay in hardening will be seen but lignification still takes place that is highly correlated with the degree this defect finally attains.

Dry heat has also been used to overcome the development of hardness during storage. Aguilera *et al.* (1982) demonstrated that dry heat processing using ceramic beads as a transfer medium allowed the continuous, large-scale roasting of beans. Subsequently, Aguilera and Steinsapir (1985) placed recently harvested Chilean gray beans in an externally heated metal drum for 3 min by which time the sample had reached an internal temperature of 105°C. Following 10 months storage at 22°C, cooked heated beans were statistically significantly, but mathematically slightly, more tender than an unheated control (397 g for the control versus 345 for HTST, as measured by the puncture test).

It will be noted in these data that a brief heat treatment produced an immediate increase in hardness. This may be a consequence of thermal activation of phytase (Chang *et al.* 1977) or, perhaps, case hardening with a concomitant reduction in water imbibition. On the other hand, the HTST process yielded an immediate decrease in hardness. The reason for this is not known but since a heat treatment had been applied and no storage effect is involved, it is unlikely to be enyzmatic in nature. Perhaps partial starch gelatinization or other processes, physical in nature, are responsible. Finally, and most importantly, it will be observed that even though the HTST treatment significantly reduced the development of hardness relative to an unheated control, 10 months storage produced a large degree of hardness in beans that had been so severely heat treated that only 2.5% would germinate. These data, if it is assumed that the samples contained no active enzymes, points strongly to a nonenzymatic component to bean hardening. If the experiments of Molina *et al.* (1976) are taken into account, a process of nonenzymatic lignification could explain these results.

Dry roasting using hot particulate media has advantages that are beneficial to stored beans. Roasting removes moisture to levels 2 to 4 percentage points below the equilibrium moisture attained by solar drying (Aguilera *et al.* 1982; Mittal *et al.* 1983). It also can be used for

pasteurizing slightly infested or mold contaminated grains and reclaiming them for human consumption (Mittal *et al.* 1981; Aguilera and Steinsapir (1985).

Irradiation. Irradiation has been considered as a means of reducing the cooking time for dehydrated vegetables. Doses for a tenfold reduction in cooking time in legumes varied from 2.0 to 4.0 Mrad (FAO/IAEA 1970). Sreenivasan (1974) and Nene *et al.* (1975) examined the potential of radiation processing to improve texture, hydration and cooking quality of legumes. A reduction in cooking time of about 40% was observed in red gram when irradiated at 1 Mrad dose. This was accompanied by higher solubility and increased swelling power of the irradiated starch and enhanced protein digestability.

The Chilean authors also examined the influence of irradiation on preventing hardness during storage. Treatments of 10, 50 and 100 krad were employed and although irradiated samples generally had lower hardness values than the control, there was no clear relationship between irradiation dosage and texture. This may have resulted from the use of levels lower than those normally administered to produce enzyme inactivation (Aguilera and Steinsapir 1985).

Soaking. It is known that phytate can be removed from whole dry beans by diffusion and associated enzymatic hydrolysis through soaking. Chang *et al.* (1977) found that incubation of presoaked beans in water at 60°C for 10 h lowered the phytate content by 90% by way of both mechanisms. Although this study did not include textural measurements, it is to be expected that a hardening effect would result from such a treatment. Similarly, Mattson (1946) observed that soaking or leaching of peas rendered them uncookable. Thus, although removal of phytate may improve nutritional value of beans, it also would produce the undesirable consequence of increased hardness.

Freezing. The former authors also experienced a 20% increase in phytate hydrolysis when beans were frozen before soaking. It is suggested that the formation of ice crystals during freezing ruptured membranes allowing enzyme substrate contact (Chang *et al.* 1977).

Chelation. According to the phytate-cation theory, any process that removed divalent cations or supplants them with monovalent ones would be beneficial to texture. That this is, in fact, effective is seen in the work of Rockland and Metzler (1967) who demonstrated the ability of tripolyphosphate and EDTA to reduce hardening. By the same token, the addition of divalent cations such as Ca^{++} will increase cooking time (Al-Nouri and Siddiqi 1982; Jones and Boulter 1983).

"Quick Cooking" Beans. The pioneering work of Louis Rockland resulted in the advancement of a protocol capable of reducing cooking

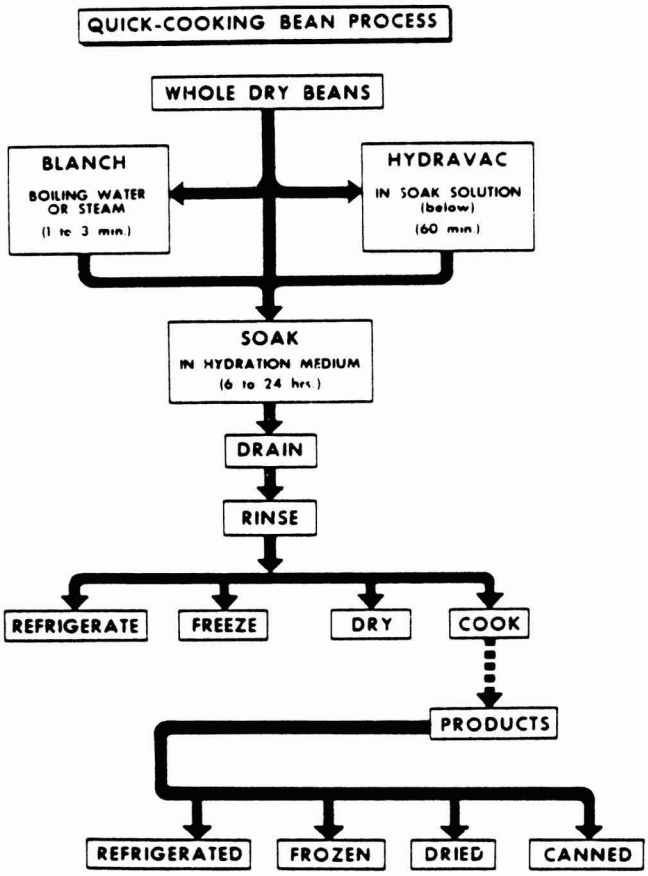

FIG. 4. FLOWSHEET FOR PREPARATION OF QUICK-COOKING BEANS
SOURCE: ROCKLAND (1978)

time of various legume varieties by 80% or more. This procedure, termed "quick cooking" represents a successful application of the principles illucidated by Mattson. Figure 4 shows a flow sheet that outlines this technology which is basically a vaccum infiltration of monovalent phosphate and other salts followed by drying (Rockland 1978). It is interesting to note that the hydration medium was selected both on the basis of ability to disperse and solubilize protein and to chelate divalent cation-protein complexes. Further work on the mechanism of this approach by Varriano-Marston and de Omana (1979) led to the conclusion that the effect is produced by ion exchange and, possibly, chelation. Divalent cations that stabilize pectates are replaced by monovalent ions or removed by chelation to phosphate groups. Silva *et al.* (1981) reported that water absorption was not significantly influenced by the mixed salts

in the soaking water but cooking times were reduced for several legume species. This technique has been applied to most common types of dry beans, most recently to broad beans (Al-Nouri and Siddiqi 1982).

Processing Alternatives for Hard Beans

Alternative processes for dry beans depend bascially on the demand for the products and on the technological level that can be afforded. Most processes presented below have not been implemented at an industrial level nor have the technologies described been applied to hard beans, nevertheless, they are options to be explored for up-grading their value.

Disruption and Dry Fractionation. It is a widely appreciated principle of food science that tough or hard commodities may be rendered acceptable by disintegration and/or cellular disruption, viz. the production of comminuted meat products from tougher cuts. This same approach has been taken with dried legumes. In some regions of the world, particularly in the Far East, legumes are dry milled to remove the seed coat leaving the split cotyledons (dhal). A method for preparing instant bean powders in which cell rupture was kept to a minimum is described by Bakker *et al.* (1973). Peas, beans or lentils were soaked, cooked, ground and drum or spray dried to remove excess moisture. Reconstitution properties were good since minimal free starch liberation occurred due to controlled cell rupture.

Dry milling causes extensive intracellular damage and has been exploited to liberate starch granules and proteinaceous material in beans, (Kon *et al.* 1977) field peas and horsebeans (Vose *et al.* 1976). For example, Aguilera *et al.* (1982) have produced bean flours by roasting, pin milling and air classification with high protein contents (about 50%) but reduced trypsin inhibitor and hemagglutinin content. This flour can be futher fractionated by air classification into a cereal analog stream (16% protein) and soy flour analog stream (43% protein); the former ingredient could be used as a replacement for wheat flour while applications for the latter include extruded products and as a protein fortificant. The principle has been implemented commercially by Pro-Star Mills Ltd. in Canada which built a 5,000 ton/year plant to fractionate pea flour into starch (two-thirds) and protein concentrate (one-third, 60% protein, dry basis) (Anonymous 1975). Thus, one way to utilize beans with textural defects is to employ further processing to yield useful products in which texture is not a determinant of quality.

Wet Fractionation. Separation of starch and protein from seeds using aqueous media is accomplished by wet milling, centrifugation of the insoluble starch granules and precipitation of the protein from the supernatant or sieving. Such wet fractionation techniques have been applied to chick pea (Deschamps 1958), field pea and fababean (Youngs

1975). In this latter case either a 90% (dry basis) protein isolate from fababean or a 63% concentrate from field pea were obtained at pilot plant scale, depending on the amount of washing. The evaporation of large quantities of water and major effluent problems are the main drawbacks of wet processing. (A similar process has also been commercialized in Canada (Woodstone Foods, Portage La Prairie, Manitoba)).

Extrusion. In most parts of the world legume foods are prepared from whole beans or splits (dhal). They may also be consumed roasted, fried, germinated or as powders in soups. Where texture is a desirable attribute whole bean powders or fractions may be structured using a combination of shear, heat and pressure. The most common method of "texturization" is an extrusion-cooking (Harper 1981). Molina *et al.* (1982) used a low cost Brady Crop Cooker to precook and form flours from black beans hardened during storage. Maximum gelatinization was achieved when beans were previously soaked in a 1% NaCl/0.75 $NaHCO_3$ salt solution. Aguilera *et al.* (1984a) reported that extrusion-texturized vegetable proteins obtained by substituting bean protein for defatted soy flour at levels of 10, 20 and 30% had similar properties as the 100% texturized soy. However, actual use of texturized bean concentrates as meat substitutes may require further improvements in functionality (Patel *et al.* 1980). Similar attempts are being carried out in Europe using field bean concentrate (Jeunink and Cheftel 1979).

Enzymes. Presumably because of the cost and potential impracticability of enzyme treatment, little work has been reported in this area. However, in 1961, Bode used an unnamed enzyme, possibly either a pancreatin or a microbial amylase, to partially convert starch to dextrins and maltose in green peas. The enzyme was added in brine and a holding period employed prior to retorting. An increase in both tenderness and flavor was reported. Purified cellulase and fungal extracts containing cellulase and/or pectin enzyme, when used in overnight soaks, decreased cooking time of legumes considerably (Morris and Seifert 1961). Much more recently, an East German patent was issued to cover the use of pectin lyase as a soaking adjunct (Bock *et al.* 1983). This process is claimed to reduce cooking time and improve sensory quality. The mechanism of this enzyme, not normally found in healthy plant tissue, is to cleave methyl-exterified D-galacturonans (pectin) between residues (Schwimmer 1981).

Animal Feeding. Secondary products of bean production are culls and hard beans. Cull dry beans consist of split, small and damaged seeds collected at harvest that are unsuitable for human consumption. Together with inedible hard-to-cook beans they may find application, after cooking, in animal nutrition as milk replacers for calves (Bell 1973), for swine feeding (Shimada 1973) and to fatten livestock and sheep (Kay

1979). Cooked beans, either autoclaved or extruded, have also been used in poultry diets (Cuca 1973; McGinnis and Capella 1973; Myer *et al.* 1982).

Effect of Storage and Processing on Nutritive Value

Sgarbieri and Whitaker (1982) have recently reviewed the nutritional properties of common bean proteins and the reader is referred to this work as well as to other reports for further information on this general subject (Aykroyd and Doughty 1964; Jaffe 1973; Bressani and Elias 1974).

The effect of hardening and processing on the nutritive value of legumes has not been extensively studied. Legumes are cooked not only to develop proper texture but also to inactivate the heat-labile anti-

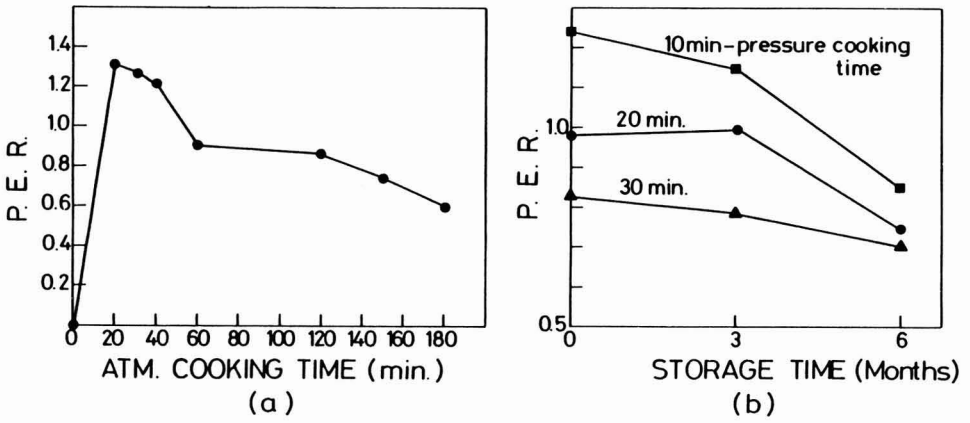

FIG. 5. A) EFFECT OF ATMOSPHERIC COOKING TIME ON THE PROTEIN EFFICIENCY RATIO (PER) OF BLACK BEANS SOURCE: BRESSANI *ET AL.* (1963); B) EFFECT OF STORAGE TIME AND PRESSURE COOKING TIME ON THE PER OF BLACK BEANS SOURCE: MOLINA *ET AL.* (1975)

nutritional factors present in the seed. Studies carried out at INCAP demonstrated that excessive cooking, however, resulted in a lower protein quality as shown in Fig. 5a. The initial rise in protein efficiency ratio (PER) is due to the rapid inactivation of trypsin inhibitors, hemagglutinins and other antinutritional factors during wet cooking (Liener 1979). After the optimum PER was reached at about 30-40 min, complex reactions between essential amino acids and carbohydrates or phenolic-type pigments begin to reduce the digestibility of the protein (Bressani 1982). Over a 20% reduction in available lysine had occurred after 2 h of atmospheric cooking (Almas and Bender 1980) or 10 min of pressure cooking (Bressani *et al.* 1963). Fig. 5b shows that the nutritive value of beans continued to deteriorate during storage while the inverse relationship between cooking time and PER value was maintained (Molina *et al.* 1975).

Table 3. Effect of time and storage conditions on hardness and nutritional quality of dry beans.

	Storage Conditions				
		25°C, 70-80% RH		37°C, 76% RH	
Storage time (months)	0	3	6	3	6
Cooking time (min)	60	85	105	180	300
Hardness (kg)	200	290	315	400	500+
PER	1.01	0.75	0.43	0.21	0.10
Digestibility (%)	62.4	61.9	57.1	59.7	54.4
Available methionine (%)	46.3	41.5	38.2	36.6	27.6
Available lysine (%)	51.6	45.8	43.0	42.0	30.1

Adapted from Antunes and Sgarbieri (1979)

The influence of storage on simultaneous changes in hardness and nutritional parameters can be appreciated in the work of Antunes and Sgarbieri (1979). Table 3, adapted from this work, shows that a combination of high temperature and high relative humidity not only had a severe effect on the rate of hardening, as discussed previously, but also lowered significantly the protein quality and the availability of essential amino acids. Even after only 6 months of storage at what could be considered benign weather conditions for the tropics (25°, 70-80% RH), the PER of beans was reduced to about 40% the original value and the available lysine, essential for complementing lysine-deficient cereal foods, suffered a 20% loss. A somewhat contradictory result was previously reported by Mlina *et al.* (1975) in which the PER of black beans descreased proportionally to storage time but total methionine and available lysine increased.

Insect infestation can also cause reduction in the nutritional value of stored legumes and make them unhygenic. For example, infested split chickpeas and pigeon peas had only 80% of the PER of uninfested samples (Parpia 1972).

Information about the effect that processing alternatives previously presented have on nutritive properties of bean products is also scant. Liener *et al.* (1976) compared the PER and digestibility of navy bean powders that had been roasted or autoclaved under optimal conditions (15 min at 121°C). The autoclaved powder (PER = 1.69) was nutritionally

inferior to the roasted product (PER = 1.92) possibly due to the somewhat better protein digestibility shown by the roasted bean. Similar results were obtained by Carvalho *et al.* (1977) who analyzed instant navy bean powders prepared by roasting in a bed of salt at 190°C for 20 s or 220°C for 10 s followed by grinding. Roasted samples, having 70-80% of the antitrypsin activity originally present, showed higher relative protein values and were more responsive to methionine supplementation than an autoclaved sample. These beneficial effects of dry roasting or nutritional quality were also seen in gray beans (Steinsapir *et al.* 1984) and cowpeas (Sales *et al.* 1984).

Dry roasting by particle-to-particle heat transfer can be effectively used for inactivating antinutritional factors in whole grains. Short time roasting (1 to 2 min) resulted in a semi-log destruction of antitrypsin factors within the temperature range of 92-126°C and the inactivation correlated well with reduction in nitrogen solubility (Aguilera *et al.* 1982). These findings are very timely in view of recent research in which lectin (hemagglutinin) activity has been detected in improperly cooked beans and even in processed legume foods. Korte (1972) reported that residual lectin activity was found in 22% of bean and maize mixtures prepared and cooked under African village conditions, resulting in signs of toxicity. More recently, increases in outbreaks of poisoning by uncooked red kidney seeds involving 870 persons were described in the UK (Gilbert 1983). Apparently some antinutritional factors present in beans may require heat treatment beyond that supplied for softening by conventional cooking.

Quick-cooking beans requiring five to six times less cooking time than regular, water-soaked beans gave similar PER values, ranging from 1.2 to 1.5 (Rockland *et al.* 1973). It should be noted that a report has suggested that reduced cooking times may lower digestibility and fail to destory all antinutritional factors (Ekpenyong and Borchers 1980) but this has been disputed (Rockland 1978).

In the area of nutritional properties of stored legumes more systematic data are needed on the effect of each spoilage vector. Further work is required on the kinetics of inactivation of antinutritional factors by heat and of nutritional losses during storage.

CONCLUSIONS

(1) The hardening of legumes during adverse storage is a pervasive phenomenon which has economic and nutritional consequences amongst some of the poorer people in the world.

(2) The mechanisms responsible for this defect are poorly understood but they might have an enzymatic and a nonenzymatic component.

(3) High temperatures and humidities accelerate the process. Hence, while the biochemical mechanisms are being ellucidated, empirical kinetic studies can be used to predict hardening under various conditions and to devise accelerated storage tests for new processes.

(4) In the short term most of the efforts in postharvest handling of beans and other legumes should be concentrated in generating recommendations for small farmers and government officials that minimize storage losses. These should include ways to physically protect beans from insects and textural changes by controlled heating, drying, packaging, etc.

(5) In the long term further studies should be performed on the utilization of damaged legumes, the effect of processing and storage on the nutritive value and the kinetics of cooking, processing and storage. This information could then be used to maximize the utilization of the legume production around the world while minimizing physical and quality losses and energy consumption.

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PEELING OF YAMS FOR PROCESSING

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ABSTRACT

White yam (Dioscorea rotundata) *lye or flame peeled were evaluated for quality characteristics and peeling loss in comparison to hand peeling. Lye concentration (15-20% at 98°C with a dipping time 3-5 min) effectively removed the histological peel as the flame method, (flame temperature was 857°C and exposure time was 9 min) with a peeling loss of 4% which was significantly lower than for hand peeling. Fresh yams were more readily peeled by these methods than stored yams. The yams peeled by lye or flame when cooked were quite acceptable as hand peeled yams. The adaptability of these methods for industrial scale up are examined.*

INTRODUCTION

Yam (*Dioscorea spp*) is an important root crop in the diet of many people in West Africa. Yam flour and instant pounded yam flour are the major processed products obtained on small scale from yam products (Onayemi and Potter 1974). The utilization of yams for chips and other products is limited by the labor required for peeling and raw tubers. Currently hand peeling is employed to peel yams, cassava and other tropical fruits and vegetables in many industries operating in Nigeria. Hand peeling is operationally labor intensive, wasteful of the material and costly as it raises the unit cost of the product.

Where large quantities of raw materials are to be peeled, hand peeling is restricted to the finishing stage like trimming, and has almost been replaced by the application of hot lye solution, mechanical devices, steam, flame, and hot air (Graham *et al.* 1964; Adams *et al.* 1960; Woodroof *et al.* 1942; Hoover 1974; Boyen 1960; Atkins and Strachan 1950).

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Although lye peeling has been successfully used for all sizes and shapes of fruits, vegetables and root crops, the effectiveness on the peeling of a commodity is determined by the lye concentration, temperature of the solution and immersion time. Rivera-Ortiz and Gonzalez (1972) reported the lye peeling of fresh yam (*Dioscorea alata*). Ngoddy and Wuderman (1976) developed a method for lye peeling fresh cassava tubers, Mazzola (1942) lye-peeled potatoes by dipping them for 10 s in a 53% lye solution at 148.5°C. Other commodities like apples, pimientos, carrots and sweet potatoes have also been successfully peeled with lye solution. However, there are major drawbacks of the lye peeling operation: effect of the lye on the product quality, risk of handling a high concentration of caustic soda at the operating temperature and use of large volumes of water for the removal of the loosened-peel which causes environmental pollution. Efficiency of lye peeling has been improved by the addition of wetting agents (Schultz and Smith 1968) and dry caustic peeling had been reported to reduce environmental pollution associated with the use of Wet lye solution (Lee and Downing 1973).

As high temperature has been found to be beneficial in the peeling process and has been used for some commodities, it was thought that flame peeling might be adopted for peeling yam tubers without the disadvantages associated with the use of lye. In the flame peeling operation, the thermal application causes a weakening of the contact between the histological peel and the flesh so that the final peel removal by brushing is made less tedious. For efficient peeling the surface is exposed uniformly to the flame and adequate steam pressure is developed which puffs the skin and loosens the intercellular connection between the skin and the cortex without rupturing the skin. Yam tubers have irregular shapes and sizes which make them unsuitable for mechanical peeling.

To our knowledge there are not many reports of comparative studies on the different methods of peeling yam tubers that commercial processors could adopt so as to improve their operation or reduce labor cost on production. This study was undertaken in order to evaluate the effectiveness of lye and flame peeling on white yam (*Dioscorea rotundata*). Another objective was to compare the influence of the peeling methods on the yield and product quality.

MATERIALS AND METHODS

Source of Yam

White yam (*Dioscorea rotundata Poir*) which is the most popular and widely cultivated of all the yams, was used. The yams were either freshly harvested or tubers stored for 3 months in local barns and were in various

sizes and shapes. Lye solutions were prepared in Dixie Canner lye-bath at concentration of 10, 15, 20, 25% using sodium hydroxide pellets of 85% purity and steam heated at 100°C ± 5°C. Prior to peeling 20-30 kg lot of the yam tubers was washed and divided into two portions. One lot was immersed in the lye solution for a predetermined time and withdrawn from the solution. The tubers were washed with sprays of cold water and scrubbed with a brush in order to remove the loosened peels. The wash water was tested for residual caustic soda by titration with phenolphthalein in order to determine the amount of sodium taken up by the tubers.

The second lot of yam tubers were washed with hot water in order to bring the temperature to near the lye solution, then dipped in lye bath for a predetermined length of time, and treated as the previous tubers.

The stored tubers were also peeled with lye solution in a similar manner described for the fresh tubers. The total weight loss was recorded as the difference between the unpeeled and peeled tubers.

An experimental batch-operating flame-peeler was devised. This was necessary since there was no commercial peeler that could accommodate the irregular shape and size of the tubers. The experimental set-up is shown in Fig. 1. One of the main features of the equipment is the holding section comprising of spring-loaded holders with tapered ends — the centering devices which support the tuber horizontally during rotation about the longitudinal axis as shown in the figure. The angular velocity of the rotating tubers was varied between 20-120π radian per minute, while the exposure to flame varied between 3 and 15 min. The tubers diameters varied between 75-105 mm. The equipment was enclosed leaving openings for fresh air and exhaust gases.

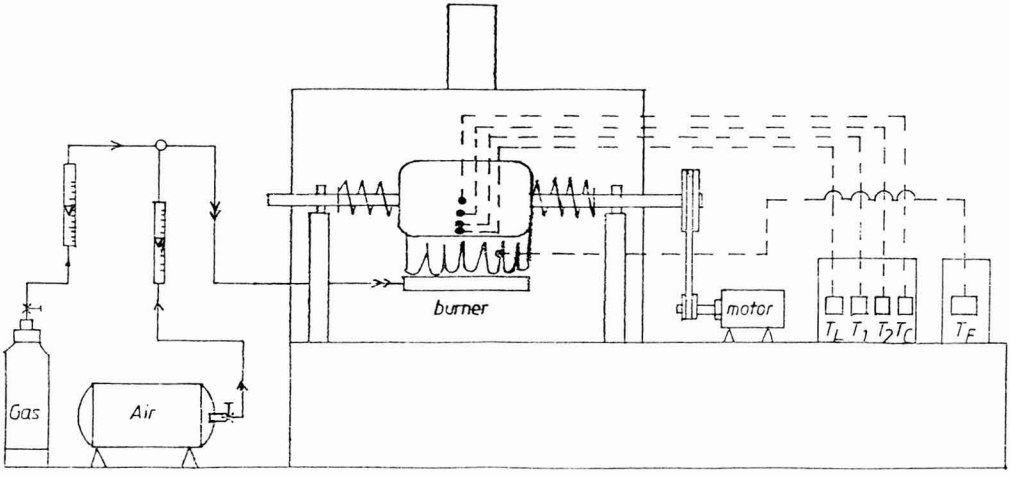

FIG. 1. EXPERIMENTAL SET-UP OF THE FLAME PEELER

Uniformity of shape and size is essential for mechanization of processing operations. The irregularity of the shape was reduced by slicing the tuber into portions with fairly uniform diameter as suggested by Ezekwe (1975). Temperature profile into the tuber was measured at various points within the tuber immediately at the end of the exposure with thermoscouple. The flame temperature was recorded with a ceramic-shielded Ni Cr-Ni thermocouple.

The fresh and stored tubers were flame-peeled and the skin was brushed. Peeling loss was tabulated as for lye-peeled tuber.

Effect of the Peeling Process on Sensory Quality of Cooked Yam

Sections of tubers peeled with lye and flame were cooked until soft and submitted to a 10 member taste panel for evaluation against hand peeled (controls) using a 5 point intensity scale where 5 is considered acceptable and 1 is not acceptable. The scores were analyzed for significance during Kramer's test (Kramer and Twiggs 1970).

RESULTS AND DISCUSSION

Lye Peeling

The fresh yam tubers were immersed in 10, 15, 20 and 25% lye solution for 8, 5 and 3 min, respectively, while the tubers which had been washed with hot water were dipped in lye solution of the same concentration for 5, 3 and 2 min. The stored yam tubers required a longer dipping time and higher lye concentration for peeling than the fresh tubers. The effectiveness of the peeling operation using different concentration of lye and dipping time for the tubers is shown in Table 1. The results showed that the stored tubers (data not presented) were more difficult to peel with lye solution than the fresh tubers. Similar observation had been reported with the water yam (Rivera-Ortiz and Gonzalez 1971). In the stored yam, the final removal of the peel was not as easy as the fresh tubers probably because the peel hardened during storage in order to protect the tubers from losing moisture (Gooding 1960). In the fresh and stored tubers, both heat rings and dark-brown patches were observed. The intensity of these defects increased with the concentration of the lye solution and were more pronounced with the stored tubers. The comparison of the penetration of sodium into the outer and the inner layers of the lye-peeled tubers showed that among the tubers, there was no appreciable difference in the retention of sodium on the outer surface and the inner layers of the peeled tuber. The sodium content of the hand peeled tuber was about 20% of the value for the lye peeled tuber. (Table 2). These sodium levels were quite

Table 1. Data showing comparisons of peel loss of fresh tubers different conditions

Lye					Flame		
Conc (%)w/v)	Dipping time (min)	Peel loss(%)	Visual appearance	Temp. °K	Exposure time (min)	Peel loss(%)	Visual appearance[1]
10	3	6.2	poor	830°C	3	2.82	poor
	5	10.8	fair		6	3.41	poor
	8	15.5	Good		9	4.52	poor
					12	4.80	Fair
					15	5.00	Fair
15	3	6.5	Fair		3	3.80	Poor
	5	11.2	Good	850°C	6	4.00	Poor
	8	16.7	Very good		9	4.69	Poor
					12	5.00	Fair
					15	5.21	Fair
20	3	6.9	Poor		3	2.37	Fair
	5	11.9	Good	860°C	6	3.20	Good
	8	17.1	Good		9	3.72	Good
					12	5.43	Fair
					15	6.13	Fair
25	3	7.3	Poor		3	3.50	Fair
	5	11.3	Poor	870°C	6	4.20	Good
	8	17.0	Fair		9	5.40	Fair
					12	7.1	Poor
					15	8.0	Poor

[1]Poor = Tubers with many unpeeled patches, and/or excessive lye penetration or burnt patches
Fair = Tubers retaining minor patches and toughened surface.
Good = Tubers with peels easy to remove
Very good = Tubers fully peeled.

low and quite harmless since in ordinary cooking, sodium chloride is normally added for flavoring.

The effectiveness of the flame peeling of the tuber was dependent on both the flame intensity, exposure duration, distance between the flame and the tubers and moisture content in the tuber.

As water vapor is involved in loosening the peel when exposed to the flame, temperature in the neighborhood of 857°C have been found to be very effective in the flame peeling process. While sufficient heat was required for the moisture and vapor movement to the contact between the skin (histological peel) and the cortex, heat penetration beyond the cortex is not desirable and this was controlled by limiting the exposure time to a period of 3-6 min for the fresh tubers and a maximum period of 6-9 min for the stored tubers, while ensuring that the tuber was rotated.

Higher temperatures and exposure duration of the tubers caused the peeled yam to have a yellowish to brownish color and a burnt appearance which was difficult to brush off with the jet of water. This was particularly noticeable in the stored tubers.

Table 2. Average peeling losses, uptake of sodium and water usage form[1]

	Peeling Methods		
	Lye[2]	Flame[3]	Hand[4]
Weight of tubers (kg)	30	30	30
Peel loss (%)	12	4	10
Yield of tuber (%)	88	94	90
Sodium content (ppm)[5]	620	120	118
Amount of water used for cleaning (ℓ)	25	14	12

[1]Loss as percent of initial weight for 10 yams.

[2]Lye concentration 15 percent, 98°C, dipping time 5 min. This lye concentration was used as it gave the optimum conditions for tubers tested.

[3]Data obtained from optimum flame peeling condition for tuber 100 mm diameter (857°C, exposure time 9 min, angular velocity 80 rad/min).

[4]Careful hand peeling, after slicing the yams into pieces about 5 cm thick.

[5]Sodium content was measured for the outer layers of the peeled tuber.

Fresh yam tubers were in general less difficult to peel than the stored tubers probably because the high water vapor in the fresh tubers at the temperature of the flame allowed the skins to be more readily removed than in the stored tubers. The heat ring developed with the stored tuber was a major source of loss. Table 2 shows peeling losses in lye and flame peeling in 5 experiments when compared with extremely careful hand peeling as normally carried out in a kitchen using tubers of uniform sizes. In considering the peeling loss the ease or difficulty of peel removal and the quantity of water used in brushing off the loosened peel must also be noted. Lye peeling required about twice the quantity of water to brush off the peel than the flame peeled tubers. In terms of efficiency or effectiveness of the peeling operation, lye peeling of the fresh tuber was easier to accomplish since the stored tubers required a high lye concentration for penetration into the corky layer that has developed in storage.

Effect of Peeling Methods on the Sensory Evaluation of the Cooked Yam

Sections of the tubers which were peeled by hand, lye or flame were cooked to doneness and submitted to a 10 member taste panel for evaluation using a 5 point scale where 5 is considered very acceptable and 1 is not acceptable. The results obtained from the sensory evaluation tests, Table 3, showed that the texture and flavor of the lye-peeled fresh tubers were equally as preferred as the flame and hand peeled tubers. Overall, the data on the sensory evaluation of the cooked did not indicate any preference of one peeling treatment.

Table 3. Taste panel scores for the peeled yams[a]

	Peeling methods			
Attribute	Lye	Flame	Hand	S.D.
Texture	3.0	4.0	4.0	± 0.817
Color	3.0	3.0	3.2	± 0.566
Flavor	3.0	3.5	3.5	± 0.624
Overall acceptability	4.0	3.5	4.0	± 0.624

[a] Based on a 5 point score where 1 = unacceptable, 5 = acceptable. The scores represent the average of 3 tasting sessions for the fresh yams. The scores shows no significant differences among the treatments.

CONCLUSION

The effectiveness of lye and flame peeling method were compared with hand peeling of fresh and stored yam tubers. Fresh tubers were more readily peeled than stored white yam with a lye concentration of 15-20% at 98°C for 3-5 min. The flame peeling method was more adaptable to fresh yam and was dependent on the flame intensity, exposure time and distance from the flame. Rotation of the yam prevented heat ring damage and discoloration. Flame peeling could be set up in areas where caustic soda is expensive as in many rural communities, in Africa since cheap labor is not readily available in these areas. The cooked tubers were highly acceptable and shows that these peeling methods are quite feasible for industrial application.

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KEEPING QUALITY OF EGGS PACKAGED IN ACRYLONITRILE POUCHES[1]

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ABSTRACT

A comparative study was conducted on quality and shelf-life of fresh shell eggs stored at room temperature with four different treatments (not-packaged, packaged in air, packaged with 15% CO_2, and oil coated). Another group, oiled and stored at refrigeration, was used as control. There was a decrease of interior quality as storage day increased but the greatest decline was observed for the not-packaged group which had the highest albumen pH and greatest weight loss. The percent weight loss of an individually packaged egg in a high barrier pouch was about 40-50% less than those not-packaged. No significant difference in Haugh unit was found between the packaged systems and the oiled plus refrigeration. It was concluded that controlled atmosphere is the most efficient method in preserving egg quality at room temperature for a period of 7 weeks.

INTRODUCTION

The factors associated with extent of shell egg quality loss are time, temperature, humidity and handling (Kamel *et al.* 1980; Heath 1977). Several methods of altering the environmental condition of the egg have been used to prolong its storage life.

For the last decades, refrigeration has been the primary method of retaining shell eggs market quality. Stadelman *et al.* (1954) compared

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quality of eggs marketed with and without refrigeration. They demonstrated that refrigeration helped to maintain egg quality for 12 days at near the initial level when eggs left the farm. Cold storage, however, is not an ideal method for the preservation of eggs. In addition to the cost of energy, a flavor characteristic of stored eggs could develop (Gross *et al.* 1947; Romanoff and Romanoff 1949).

Oil coating of the shell has also come into common usage to increase shelf-life of eggs. Yamauchi *et al.* (1979), however, reported that problems of lipid peroxidation and migration into edible part are inherent when the oiled shell method was used.

The introduction of a small amount of carbon dioxide, CO_2, into the storage atmosphere to improve the quality of eggs was first suggested by Sharp (1929). Cotterill and Gardner (1956) have reported that storing eggs in a low concentration of CO_2 at 21.1-26.7°C produced eggs with a quality as good as those under normal atmospheric conditions at 10°C. Commercial use of CO_2 in the preservation of eggs has become fairly extensive (Stadelman and Cotterill 1977).

Control of moisture and gas composition within a package has been employed frequently to extend keeping quality of many foods such as meat, fruits and vegetables. In some cases, the packaging could replace some of the refrigeration requirement. Unit package employing modified or controlled atmosphere to extend storage life of shell eggs would be beneficial not only in reducing the complicated and expensive equipment necessary for maintaining the gas chamber but also offering an opportunity for energy saving.

Few investigations have concerned the use of packaging to extend the storage life of fresh shell eggs. An early study by Swansan and Helbacka (1954) followed the changes in the interior quality of shell eggs packaged in overwrapped cartons containing an atmosphere enriched in CO_2. They reported that albumin quality loss can be minimized for over six weeks when stored either at 50°F or at a temperature of 75 to 86°F. On the other hand, Fletcher *et al.* (1959) found no benefit to adding CO_2 to 5-dozen lots stored in plastic bags and maintained at a lower temperature of 30°F at 80% RH. Besides the differences in storage condition, packaging method and barrier properties of the film used could also affect the final results.

In this work we evaluated the effectiveness of individual packaging with a high gas barrier film in maintaining quality characteristics of fresh shell egg at room temperature.

MATERIALS AND METHODS

Materials

Acrylonitrile copolymer film, 2 mil thickness, was obtained from Greenway Industries Corporation (Somerset, NJ). Pouches of size 4 in. × 3 in. were made from the material. A small drop of silicon sealant was cured on each pouch surface to serve as gas flushing and sampling port.

White Leghorn chicken eggs, laid between one to two days prior to use were obtained from the Rutgers University Poultry Farm.

Methods

Sample Preparations. Cleaned eggs were subjected to one of the following treatments: (1) Packaged in the acrylonitrile copolymer pouch with one egg per pouch; (2) Packaged in similar pouch where initial carbon dioxide (CO_2) concentration of the headspace was adjusted to 15% (V/V); (3) Not-packaged, and (4) Oil coated by immersing in a bath of vegetable oil (corn) for 3 s at room temperature (23°C) then drained.

All samples from above treatments, 1 to 4, were stored at 25°C ± 1° at 25% RH ± 2% to provide for temperature stress and moisture loss.

Another group, (treatment 5) of the oiled samples were kept in a refrigerator (5°C + 1°) to simulate retail or home storage condition.

At intervals, eggs were randomly picked from each group for quality evaluation.

Percent Weight Loss. Eggs were weighted with an analytical balance. Percent weight loss was expressed by the difference between initial fresh egg weight and weight of the same egg at sampling divided by the initial weight.

Haugh Unit. Interior egg quality was determined by Haugh unit measurement as described in the USDA Egg Grading Manual (1968).

Albumen pH Value. Egg white separated from the yolk was measured for pH using a Fisher Accumet Model 320 Expanded Scale Research pH Meter (Fisher Scientific, Pittsburgh, PA). Care was taken to ensure that the albumen was not contaminated by the yolk contents, particularly at the later stage of storage where the yolk was softest and easily broken.

Headspace CO_2 Concentration. 0.5 ml headspace gas sample was periodically drawn from the pouch for CO_2 analysis with a Varian 2700 gas chromatograph (GC). The conditions for GC determination are as follows: Detector: Thermal conductivity; Column: TRI (Alltech Associates, Inc. Deerfield, IL); Column Temperature: Ambient (23°C); Carrier Gas: Helium; Flowrate: 120 cc/min.

Film Permeabilities. Barrier properties of Acrylonitrile copolymer film at CO_2 and water vapor were determined by the method of Gilbert and Pagaz (1969).

Data Analysis. Data were analyzed by analysis for variance and regression procedure of the SAS program (SAS 1982).

RESULTS

Acrylonitrile copolymer film (AN) was determined to be an excellent barrier against carbon dioxide, with fairly low water vapor transmission. Baccars *et al.* (1985) also reported that AN offers good oxygen barrier properties. Permeation constants found for AN are 0.30×10^{-4} ml mil/day/m^2/atm and for CO_2 and 0.29 g mil/day/m^2/atm for water vapor, at room temperature.

The results on weight loss show in Fig. 1 that the maximum loss was observed in samples from (3) followed by (1) and (2). The lowest rates of weight loss were observed for both (4) and (5). Samples from both packaging systems (1, and 2) were not significantly different in weight loss

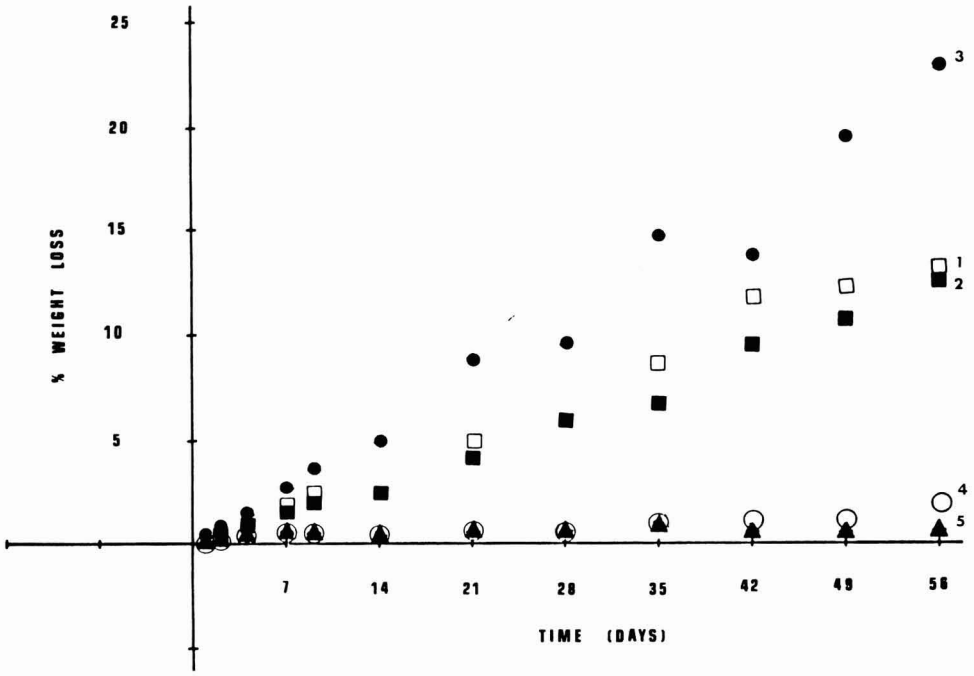

FIG. 1. EFFECT OF TREATMENTS ON % WEIGHT LOSS OF SHELL EGGS DURING STORAGE
Symbols same as FIG. 2.

(P = 0.05), and they were about 40-50% lower in weight loss than those from (3) throughout the storage.

The data on pH of albumen for the different treatments during storage are given in Fig. 2. Slight decrease in albumen pH value was found in this study for all treatments, except those from (3) where pH of the egg

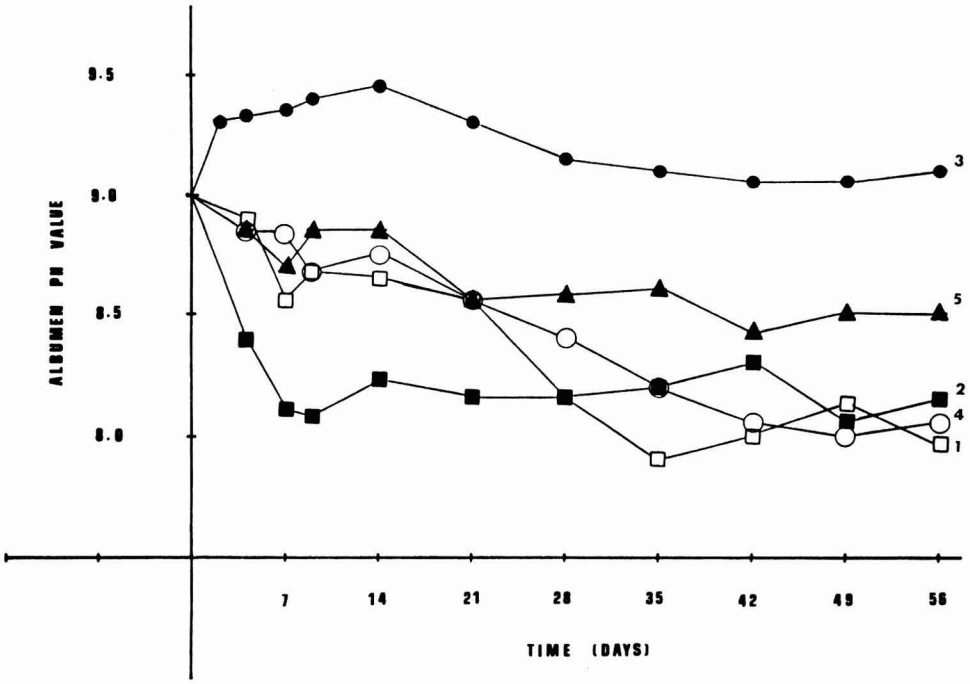

FIG. 2. EFFECT OF TREATMENTS ON ALBUMEN pH VALUE OF SHELL EGGS DURING STORAGE
(3) ● — ● not-packaged; (1) □ — □ packaged in air; (2) ■ — ■ packaged in 15% CO_2; (4) ○ — ○ oiled; (5) ▲ — ▲ oiled plus refrigerated.

white initially went up to about 9.5 and then leveled down to 9.2 after 42 days of storage.

Haugh unit scores for different treatments presented in Fig. 3 show greatest decrease in value for the not-packaged eggs (3). The interior quality of (3) dropped sharply from a grade of AA, USDA Standard of Quality, to the B grade in one week when stored at room temperature. The quality continued to decline rapidly and reached grade C after 28 days whereas samples from other treatments still maintained a B grade after storing for 7 weeks.

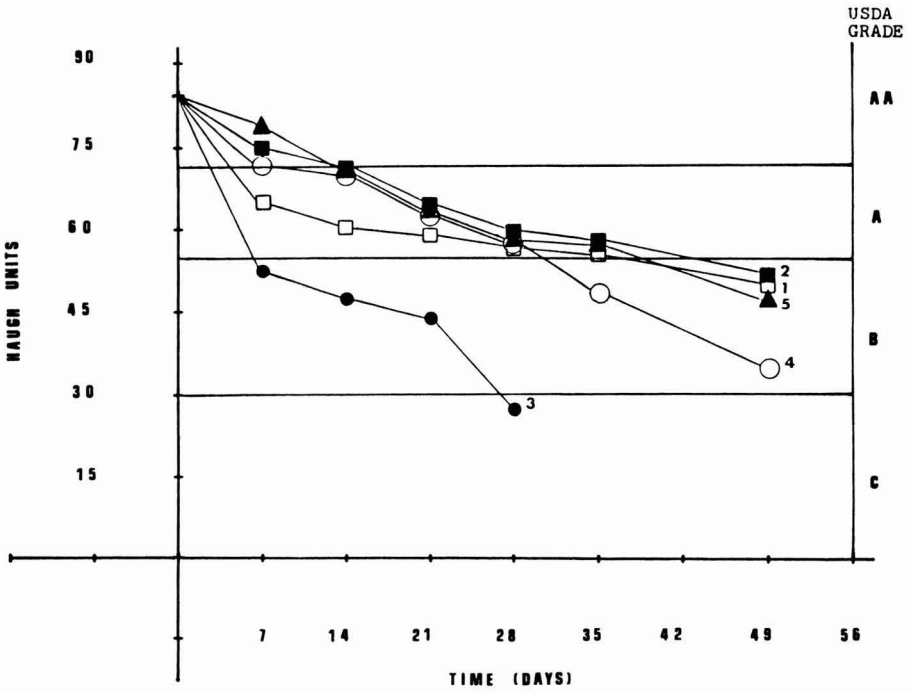

FIG. 3. EFFECT OF TREATMENTS ON HAUGH UNIT AND QUALITY GRADE OF SHELL EGGS DURING STORAGE
Symbols same as FIG. 2.

DISCUSSION

The albumen pH measured was about 9.0 for the samples at initial period (Fig. 2). This is expected since the eggs were about two days old at the time this experiment started. As soon as the egg is laid the pH of the albumen begins to increase as a result of escape of CO_2 from the egg (Moran 1937). Heath (1977) reported that the largest change in pH occurred between 0 and 3 days after laying.

There was a decrease of interior quality as the time of storage increased but the greatest change was observed for eggs from (3). The rate of deterioration of egg is closely related to the loss of CO_2 through the shell and increase in alkalinity of the egg contents (Overfield 1982). Oil coating treatment reduces the molecular transport of water vapor and gases through the pores of the egg shell. Lowest weight loss was recorded for the oil treated samples (4 and 5) which all retained some grade A quality at the fourth week of storage. The data are in agreement with the results of Lohchuba and Kumar (1971) that oiling of shell eggs reduced weight loss and preserved the internal quality of eggs for a period of one month

at room temperature. Kamel *et al.* (1980) also showed that the interior quality of oil treated eggs was significantly better than for untreated eggs even at 42°C.

Packaged eggs at room temperature (1 and 2) maintained Haugh values which were not significantly different ($P = 0.05$) from those that were oil-treated and refrigerated (5) for a period of 7 weeks. On the other hand, oiled sample (4) decreased to the lower B grade after 49 days of storage.

Headspace CO_2 concentration from the pouch samples was monitored during storage (Fig. 4). The CO_2 concentration of (2) decreased rapidly from 15% to about 3% after storing for one day. This is expected since the majority of CO_2 inside a freshly laid egg would be liberated in the first day (Heath 1977). An absorption of the gas by the egg contents would then take place until an equilibrium is established between the surrounding and CO_2 concentration within the egg. The lower albumen pH observed for (2) in the first 21 days of storage further confirmed that CO_2 is taken up by the egg.

Sharp (1929) suggested that the concentration of CO_2 necessary in the atmosphere to hold the white at pH 7.6, the pH of the albumen of a fresh

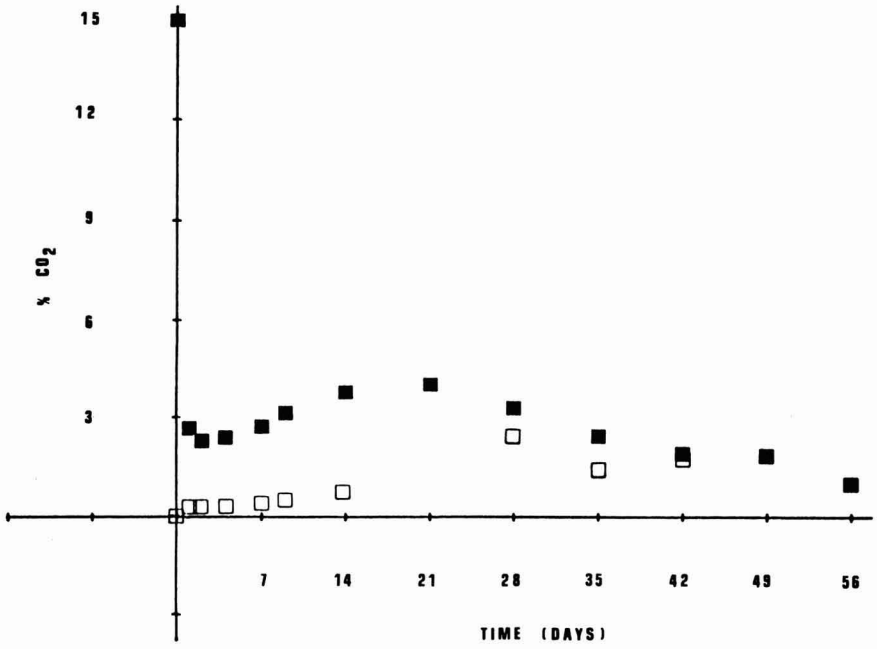

FIG. 4. CHANGES IN HEADSPACE CO_2 CONCENTRATION OF TWO EGG PACKAGING SYSTEMS DURING STORAGE
(1) □ — □ packaged in air; (2) ■ — ■ packaged in 15% $C)_2$

egg, is approximately 10 to 12% of CO_2. Smith (1931), in contrast, reported that to maintain the pH of egg albumen near its original value, the storage atmosphere should contain 3.0-4.5% of CO_2 at room temperature. Our study, however, has shown that at an atmospheric CO_2 concentration of 3%, the albumen pH value of the samples is 8.2. The amount of CO_2 movement through the egg is a function of temperature, time, and partial pressure of CO_2 in the surrounding atmosphere (Cotterill *et al.* 1958). Robel *et al.* (1985) also reported that egg integument may also control the gaseous exchange of the egg.

In our case, the addition of CO_2 into the package did not provide increased interior quality over those packaged with air. It is reasonable to believe that (1) would have been better shelf-life if the eggs had been packaged with the high barrier film soon after they were laid. In this respect controlled atmosphere (1) appeared preferable to modified atmosphere (2) in packaging the fresh shell egg individually for room temperature storage.

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SEDIMENT FORMATION IN ASEPTICALLY PROCESSED AND PACKAGED MILK

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ABSTRACT

Sediment formation in aseptically processed and packaged milk was investigated by determining initial sediment amount and sediment rate. Milkfat levels were 0.5, 1.5 and 3.2%. Processing temperature was 143°C and mean residence times in the holding tube were 0.75, 7.32, and 18.6 s. Overall heat transfer coefficients for the tubular heaters during processing were determined to provide an indirect measurement of the extent of fouling. At time intervals of 30-45 min a few packages were aseptically filled and stored at 4, 23 and 35°C for a 26 wk period. Initial sediment (≤ 1 wk) increased linearly with processing time for all process conditions. Sedimentation rates increased linearly with storage temperature. Fat level and increased thermal treatment due to increasing holding time had no significant effect on sediment formation. The formation of particles during storage was examined as both a physical diffusion type settling process and as a particle forming chemical reaction followed by settling.

INTRODUCTION

Sediment in aseptically processed and packaged (APP) milk is a visually undesirable deposit occurring in the stored product. Settling materials have been associated with a chalky mouthfeel (Burton 1969). This sedimentation results from denaturation of milk proteins or, sometimes, precipitation of salts (Hsu 1970; Samuelsson and Holm 1966;

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Andrews and Cheeseman 1972). Burton (1968) postulated that salts and protein crystallize out of milk at high temperatures and appear as deposits on the heat exchanger wall or as sediment in the packaged product. Short (1969) speculated that sediment is caused by erosion of the fouled layer.

Several factors during processing and storage have been shown to affect sedimentation. Several investigators have indicatd that more severe thermal treatment increases the rate of sedimentation (Ramsey and Swartzel 1983; Samuelsson and Holm 1966; Swartzel 1983b). Swartzel (1983b) established a predictive expression for relating thermal treatment change due to fouling to sedimentation rate changes for lowfat milk. Burton (1967) and Bell and Sanders (1944) found that fouling increased as milkfat level increased. Lund and Sandu (1981) noted that although fats do contribute to fouling their role is a minor one. They postulated that fat globules participate in the fouling reaction either as an individual species adsorbed at the heat exchanger interface or through the lipo-protein system at the globule surface. Noting the high activity of proteins in fouling they felt that the latter mechanism was more likely.

The role milkfat level plays on initial sedimentation is not well understood. However, it has been shown that sedimentation increases with storage time and storage temperature (Corradini *et al.* 1967; and Ramsey and Swartzel 1983). The effect of milkfat level on this increased sedimentation during storage has not been determined.

This study was designed to investigate the relationship between source of thermal treatment (heating sections and nonheated holding sections) and sedimentation in stored aseptically processed milk. In addition, the effect of milkfat concentration, level of thermal treatment, storage time and storage temperature on amount of sediment and sedimentation rates were investigated. Aspects of heat exchanger fouling behavior and erosion, as related to product sedimentation, were also examined.

MATERIALS AND METHODS

A composite of winter milk from three North Carolina State University herds was standardized at approximately 0.5, 1.5 and 3.2% fat. Prior to processing, samples were collected and analyzed quantitatively for milkfat, total solids, O_2, colony forming units (CFU), and pH. All milk was processed in an ultra-high-temperature tubular processing system (Unitherm model XLV, Cherry-Burrell, Cedar Rapids, Iowa) as shown in Fig. 1. After preheating to 74°C in a plate heat exchanger, product entered the timing pump where the flow rate was maintained at 2.84×10^{-4} m^3/s. Throughout the study, product discharge temperature

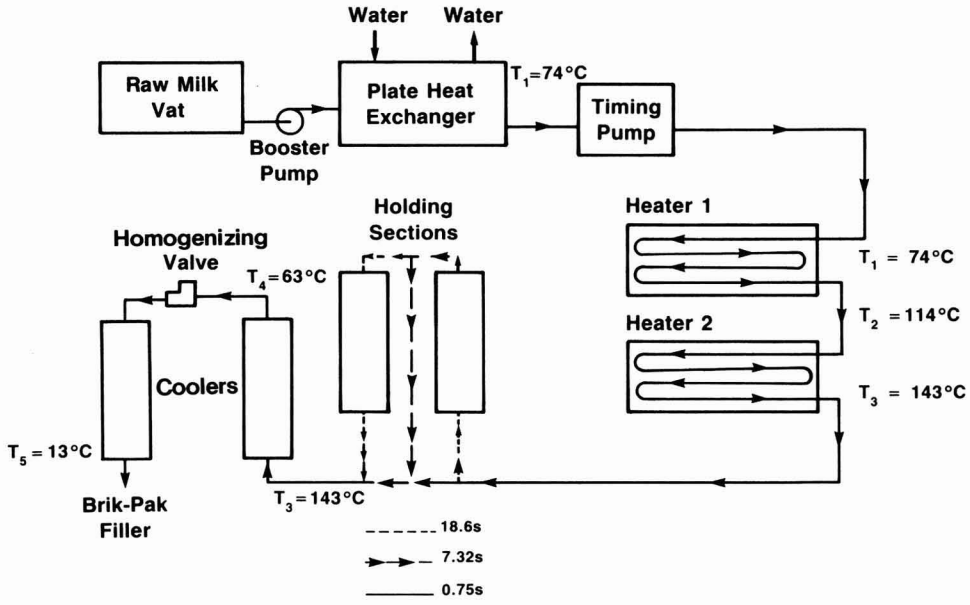

FIG. 1. FLOW DIAGRAM OF THE PROCESSING SYSTEM

from Heater 1 was held at 114°C, and from Heater 2, at 143°C. Shell side steam pressure was controlled to maintain constant product temperatures.

Thermal treatments were varied by controlling mean residence times for the holding section at 0.75, 7.32, or 18.6 s. All product was cooled to 63°C, homogenized at 20.7 MPa, and further cooled before packaging aseptically in a Tetra Pak asetpic filler (model AB3-250, Tetra Pak, Dallas, TX).

All temperatures in Fig. 1 were measured by copper-constantan thermocouples and recorded at 5 min intervals using a data logger (Model 9300, Monitor Labs, Inc., San Diego, CA). One run for each holding time/fat level combination produced nine total runs. A few packages were filled at a time every 30 or 45 min during 120 min total processing time for each run. Samples from each run and each package time were stored at 4, 23 and 35°C.

Between runs, the system was thoroughly cleaned by circulating: (1) alkali solution (LIQUA-BRITE X, Diversey Wyandotte, Wyandotte, MI) for 1 h at 82°C; (2) hot water rinse; (3) acid solution (UHT acid, Diversey Wyandotte, Wyandotte, MI) for 1 h at 71°C; and (4) hot water rinse. Fouling resistance values were determined as described by Fischer *et al.* (1975) using the equation:

$$R = 1/U - 1/U_o \quad (1)$$

Sedimentation measurements were made by modifying the method of Ramsey and Swartzel (1983). Containers were carefully handled to minimize disruption of sediment in the package. After milk was poured out of the container, the top portion of the container was removed 4 cm from the bottom. The inverted carton base was allowed to drain for 15 min. Folds in the carton base were opened to permit exposure of all sediment for rapid drying. The carton base, with sediment, was dried in a lab hood for 48 h, then placed in an environmental chamber at 23°C with relative humidity of 48% for 8 h. Samples were weighed. Each carton was opened to a flat sheet and washed to remove all sediment. They were dried again for 24 h in a laboratory hood and 8 h in the environmental chamber. The clean, dried cartons were then weighed. Sediment was determined by difference in weight of the dried carton with and without sediment. Stored samples were analyzed for sediment at 6, 13, 20, 27, 41, 55, 69, 83, 97, 111, 125, 139, 153, 167 and 181 days of storage. Duplicates for each combination of fat level, heat treatment, processing time, storage temperature and storate time were analyzed.

RESULTS AND DISCUSSION

A high quality milk supply was furnished in most cases. There were selected standardized milks which were less than high quality. A description of the milk is given in Table 1.

Table 1. Milk supply description

	MILKS BY FAT LEVEL					
	0.5		1.5		3.2	
CFU/mL	2.2×10^4 – 1.1×10^6		1.3×10^4 – 1.0×10^6		3.8×10^3 – 3.8×10^6	
	$\bar{X}$	σ	$\bar{X}$	σ	$\bar{X}$	σ
O_2 (ppm)	10.08	0.49	9.76	1.45	9.26	0.80
pH	6.56	0.16	6.63	0.29	6.49	0.13
TOTAL SOLIDS	9.76	0.20	10.55	0.07	12.11	0.05
% MILKFAT	0.55	0.13	1.50	0.17	3.15	0.04

Linear regression models provided good statistical descriptions of the relationship of total grams sediment (gsed) to storage time (t_s) for the 6 to 181 day storage period. Models fitted were of the form

$$gsed = S_o + Srate\ (t_s) \quad (2)$$

where S_o is the intercept (g) and Srate is the sedimentation rate (g/day). The values for Srate and S_o were evaluated with respect to holding time, fat level, processing time, and storage temperature. All estimates are given by Hawran (1984).

Srate estimates were divided into 27 groups by the variables of fat level, holding time and storage temperature. Each group was averaged. Averages and standard deviations are shown graphically in Fig. 2, 3 and 4. From these figures, Srate can be seen to be temperature dependent, increasing with storage temperature. Srate differences for fat level and holding time were not apparent.

S_o estimates were examined in the same manner as Srate. Averages ($\bar{x}$) and standard deviations (σ) are shown in Fig. 5, 6 and 7. Storage temperature, fat level and holding time appeared to have no affect on S_o. The Srate and S_o estimates for various processing times were analyzed using the analysis of variance (ANOVA).

Table 2 for ANOVA of S_o demonstrates that, although a significant difference occurred between runs, most variation was due to processing time (t_p). Storage temperature (T_s) had no significant affect on S_o.

Table 2. Analysis of variance for S_o*

SOURCE	df	MEAN SQUARE $*10^{+2}$	F
RUN	8	17.60	8.34**
t_p	5	67.20	32.00**
RUN*t_p	23	2.10	3.86**
T_s	2	3.82	4.03
T_s*t_p	10	1.52	1.61
ERROR	59	0.95	

*Computations from these tables were made with more decimals than indicated and the results rounded.

**Significant at $P < (0.05)$.

Table 3 for ANOVA of Srate demonstrates that for Srate a significant different is apparent between runs, but most of the variation is caused by storage temperature (T_s).

Run variations for S_o and Srate were not due to thermal treatment or fat level as evidenced by Fig. 2-7.

Table 3. Analysis of variance for Srate*

SOURCE	df	MEAN SQUARE $*10^{+4}$	F
RUN	8	11.40	13.90**
t_p	5	0.82	1.00**
RUN*t_p	23	0.81	0.92
T_s	2	740.00	481.00**
T_s*t_p	10	1.80	1.17
ERROR	59	1.54	

*Computations from these tables were made with more decimals than indicated and the results rounded.
**Significant at $P < (0.05)$.

The relationship of total grams sediment (gsed) to storage time (t_s) with respect to differences in packaging time (t_p) and storage temperature (T_s) are shown in Fig. 8, 9 and 10.

Mean estimates of S_o and Srate were used to develop models to predict the amount of sediment in the container. In Fig. 11, S_o increased linearly with processing time. The equation for the relationship was determined as:

$$S_o = 4.52 \text{ X } 10^{-4} t_p + 0.0298 . \quad (3)$$

The linear relationship of Srate, after six days, and storage temperature is shown in Fig. 12 with constants determined as:

$$\text{Srate} = 0.293 \text{ X } 10^{-4} T_s + 1.20 \text{ X } 10^{-4} . \quad (4)$$

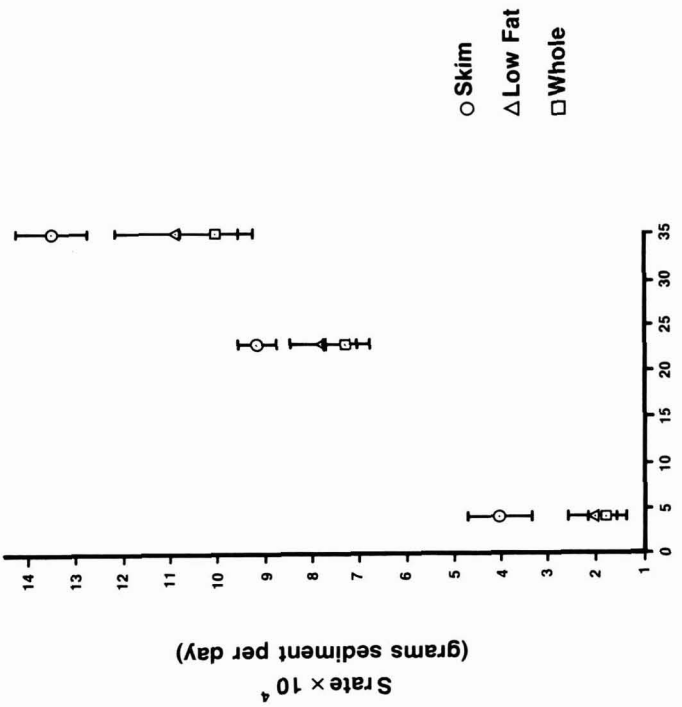

FIG. 2. EFFECT OF STORAGE TEMPERATURE (T_s) ON SRATE HOLDING TIME (t_h) = 0.75 s

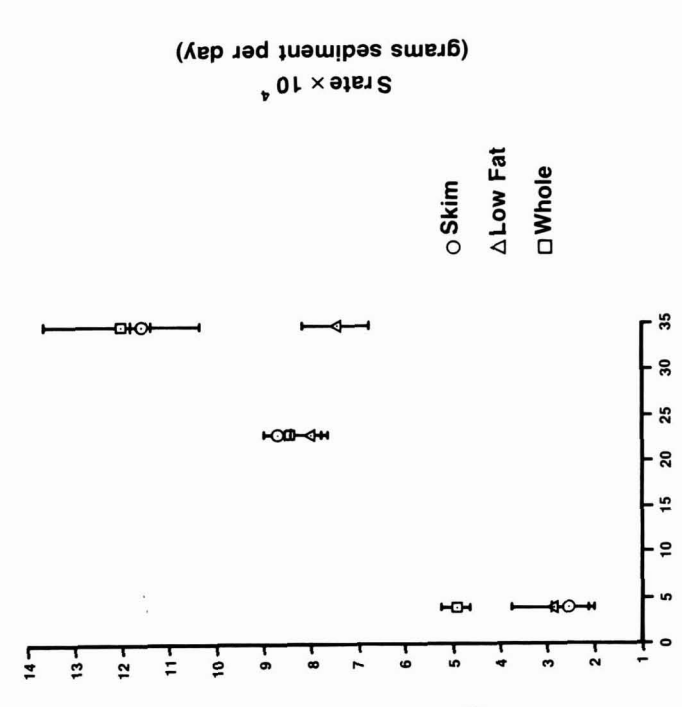

FIG. 3. EFFECT OF STORAGE TEMPERATURE (T_s) ON SRATE HOLDING TIME (t_h) = 7.32 s

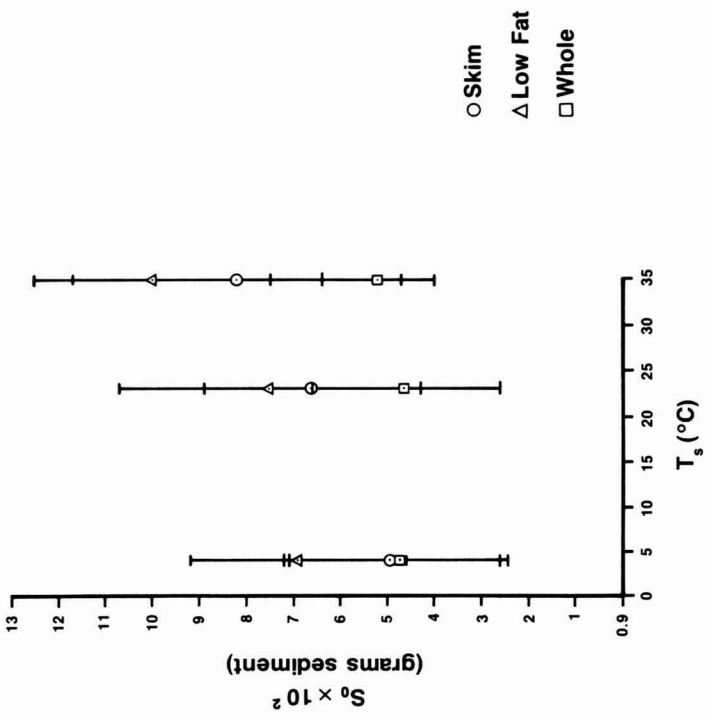

FIG. 4. EFFECT OF STORAGE TEMPERATURE (T_s) ON SRATE
HOLDING TIME (t_h) = 18.6 s

FIG. 5. EFFECT OF STORAGE TEMPERATURE (T_s) ON S_o
HOLDING TIME (t_h) = 0.75 s

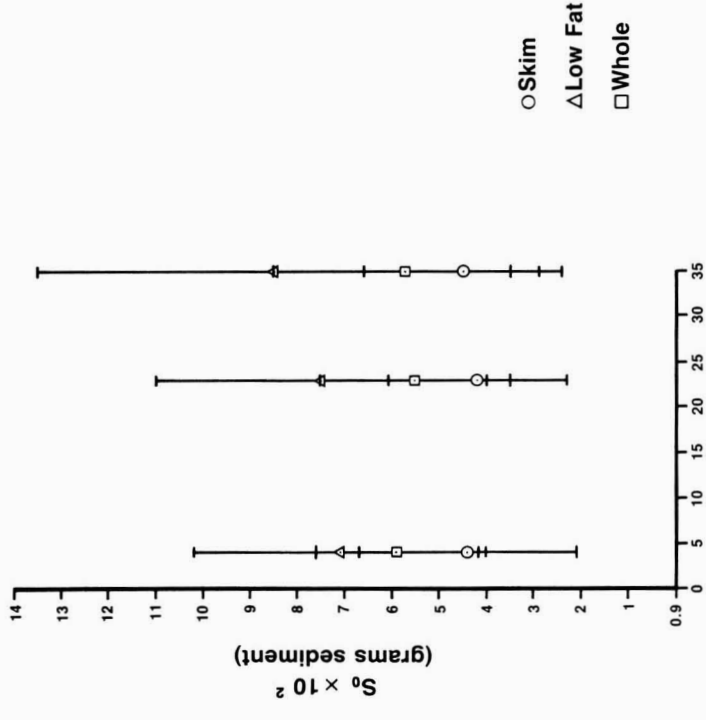

FIG. 6. EFFECT OF STORAGE TEMPERATURE (T_s) ON S_o
HOLDING TIME (t_h) = 7.32 s

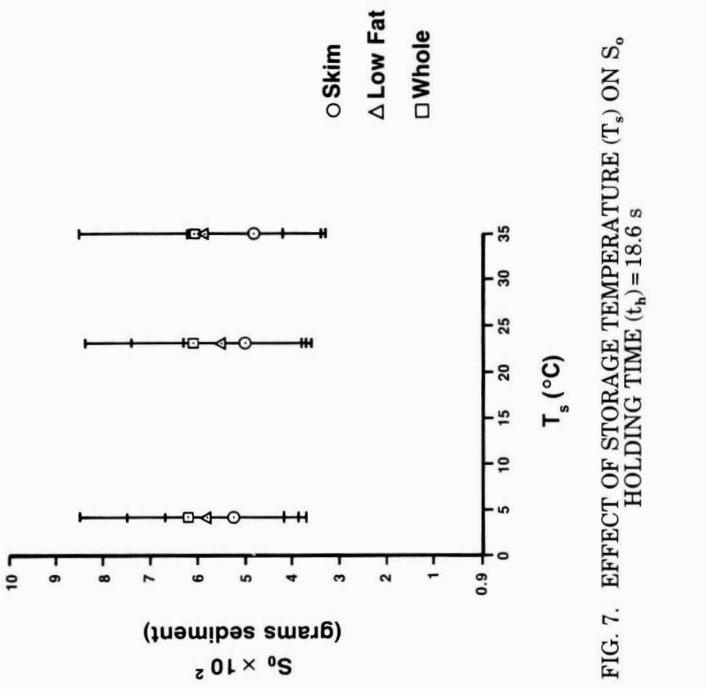

FIG. 7. EFFECT OF STORAGE TEMPERATURE (T_s) ON S_o
HOLDING TIME (t_h) = 18.6 s

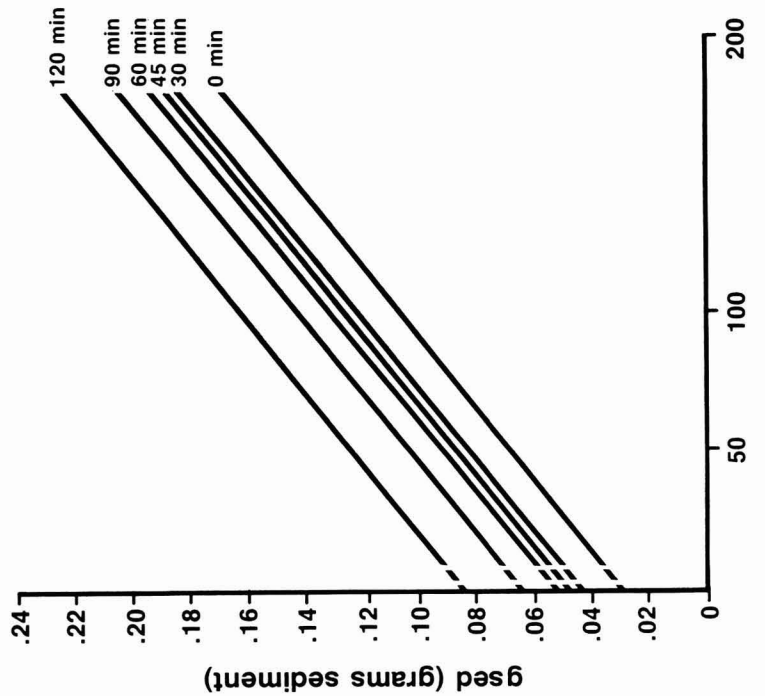

FIG. 8. EFFECT OF STORAGE TIME (t_s) AND PROCESSING TIME (min) ON SEDIMENTATION $T_s = 4°C$

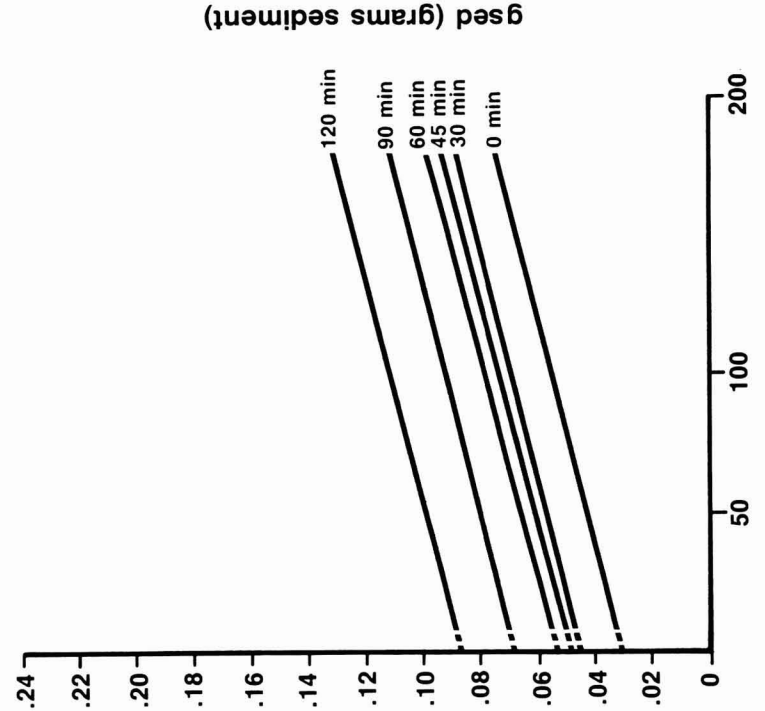

FIG. 9. EFFECT OF STORAGE TIME (t_s) AND PROCESSING TIME (min) ON SEDIMENTATION $T_s = 23°C$

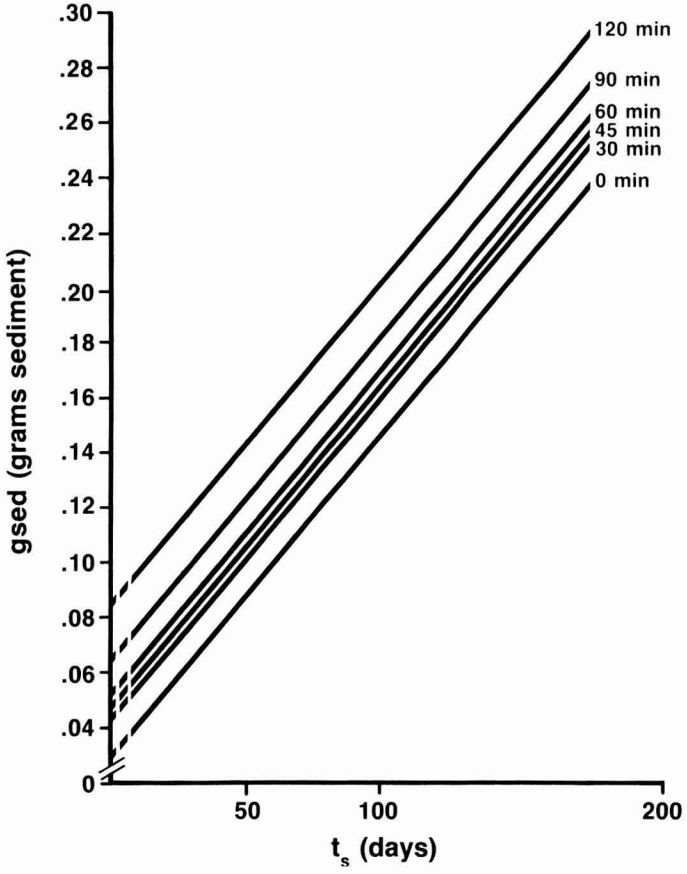

FIG. 10. EFFECT OF STORAGE TIME (t_s) AND PROCESSING TIME (min) ON SEDIMENTATION $T_s = 35°C$

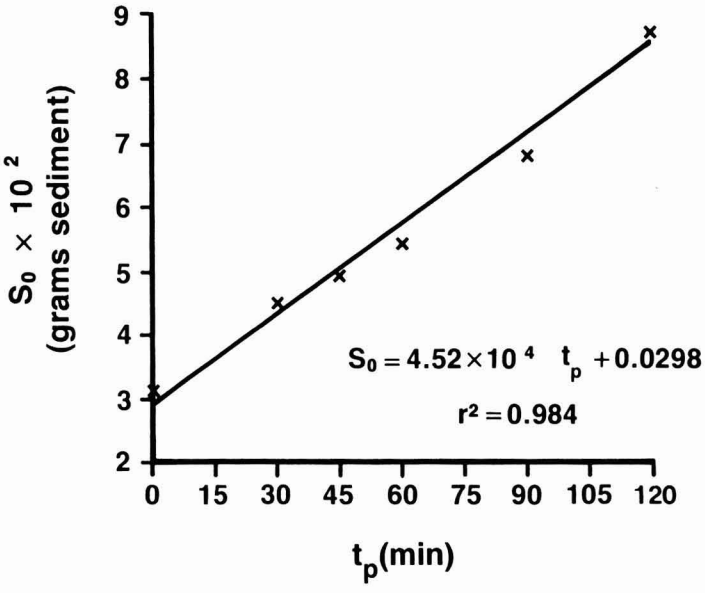

FIG. 11. S_o AS A FUNCTION OF PROCESSING TIME (t_p)

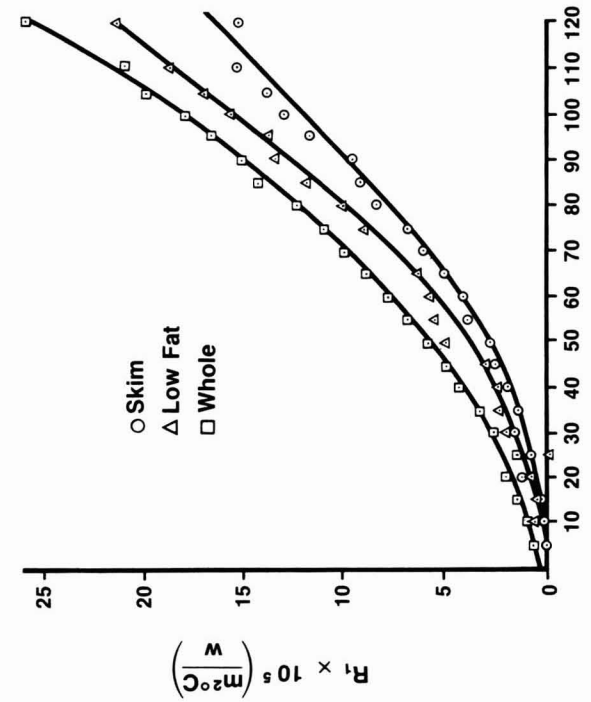

FIG. 13. FOULING IN HEATER 1

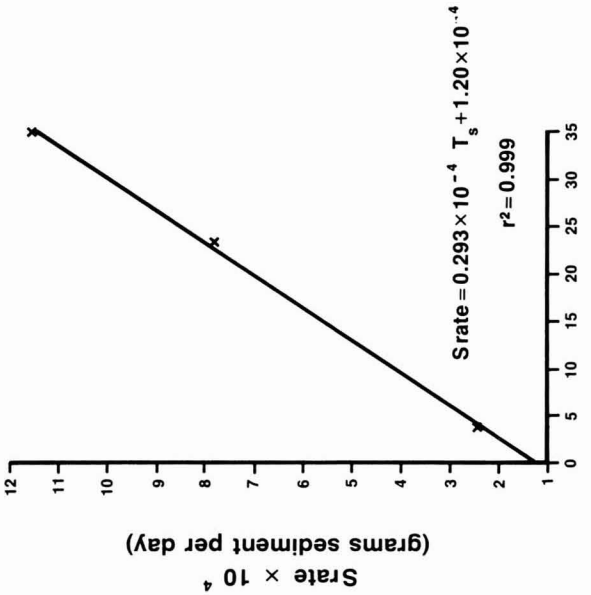

FIG. 12. SRATE AS A FUNCTION OF STORAGE TEMPERATURE (T_s)

Grams sediment (gsed) for t_p, T_s and t_s can be determined by

$$gsed = S_o + Srate\ (t_s)\ , \tag{5}$$

with substitution of Eq. 3 and 4.

Fouling was examined by plotting fouling resistance for Heater 1 (R_1) and Heater 2 (R_2) as a function of processing time (t_p). Reynolds numbers for Heaters 1 and 2 were calculated as 66,700 and 97,000, respectively, where in Heater 1 mean values for density and viscosity for the three fat levels were taken as,

$$\rho = 0.988 \text{ X } 10^{-3} \text{ kg/m}^3, \eta = 4.8 \text{ X } 10^{-4} \text{ Pa. s}$$

and in Heater 1

$$\rho = 0.977 \text{ X } 10^{-3} \text{ kg/m}^3 \text{ and } \eta = 3.3 \text{ X } 10^{-4} \text{ Pa. s}$$

(Swartzel 1982). Graphs of the fouling resistances are shown in Fig. 13 and 14, respectively. Each point represents the mean R value from three

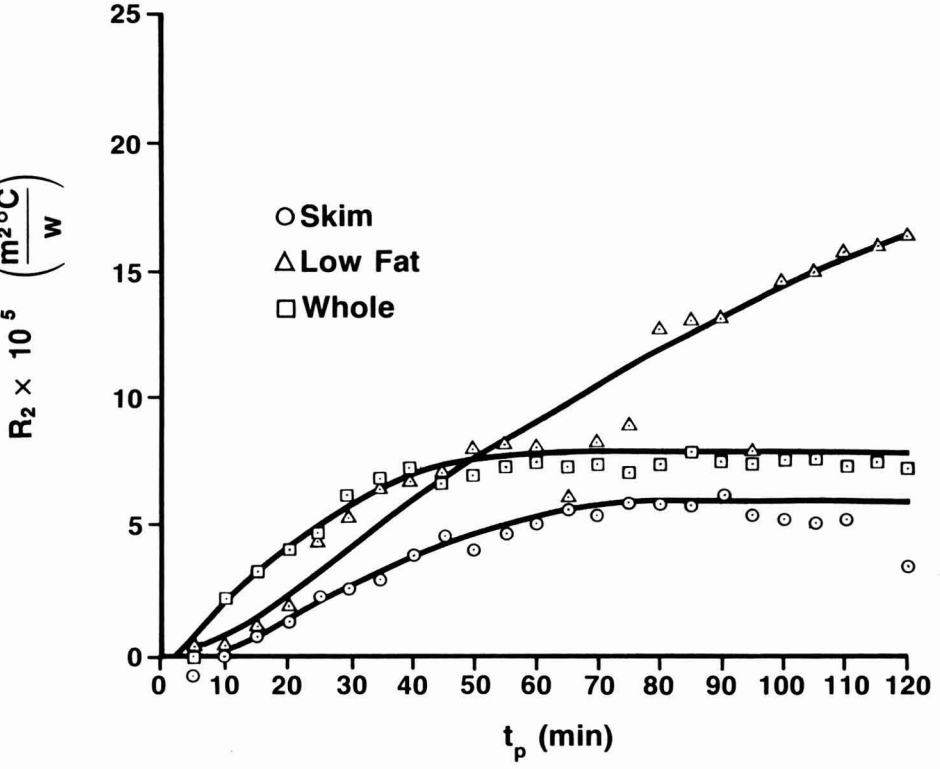

FIG. 14. FOULING IN HEATER 2

runs of the given fat level. In Heater 1, more fouling is apparent for a higher fat level. This may be due to an entrainment of fat during the fouling process as other fouling reactions such as protein denaturation and salt desolubilization are taking place. In Heater 2, more fouling occurred for whole milk than skim milk, but lowfat milk does not following the same trend.

In Fig. 13 for Heater 1 the increase in slope with time indicates that fouling rate increases with processing time. In Heater 1 the fouling deposition rate is always greater than the erosion rate. Whole and skim milk curves for Heater 2 increased and then leveled off; these curves exhibit "asymptotic" fouling behavior as described by Taborek *et al.* (1972). Asymptotic fouling behavior may indicate an increase of removal mass flux (dissolution, erosion, spalling), and/or a decrease of deposition mass flux, (Sandu and Lund 1983). Evidence of induction periods, also described by Taborek *et al.* (1972), is not strong.

Lyster (1965) found that milk which has not been preheated tended to deposit mainly protein (50-60%) in the lower temperature (100-105°C) heating sections of the heat exchanger. In the higher temperature sections, the deposits were mainly ash (70%) with all deposits diminishing near the heater outlets.

Comparing fouling of Heater 1 to that in Heater 2, there is more total resistance to heat transfer in Heater 1. This is either because more deposits may have formed in Heater 1 or the material in Heater 1 may have had a lower thermal conductivity. Considering the fouling trends found by Lyster (1965) and discussed by Burton (1968), it can be speculated that the material in Heater 1 was mainly protein and the material in Heater 2 was mainly ash. This concept is also supported by the work of Lund and Bixby (1974). They found that, by prefouling a heat exchanger with calcium-phosphate, overall heat transfer coefficients obtained with milk did not decrease over a 2 h processing run. This suggests that in Heater 2 a calcium-phosphate layer may adhere, decrease the overall heat transfer coefficient and, thus, limit further fouling by calcium-phosphate or protein.

Burton (1968) noted that deposit in the heat exchanger increased with decreased pH, increasing significantly below a pH of 6.5 This was confirmed in this study. Burton also noted that aging, with no change of pH, causes a marked decrease in the amount of deposit. Although there were marked differences in number of colony forming units per ml (an indication of aging) all milks in this study were at least 40 h in age. At this age Burton (1968) noted an increase in the deposits formed with increased age. Any effect aging played in this study was minor and could not be distinguished from the effect of pH.

Burton (1968) also stated that air content encourages deposit formation if it separates as bubbles on the heating surface, and that its effect will be eliminated if sufficient pressure is maintained. Since constant homogenizing pressure (20.7 MPA) was maintained throughout all runs, the effect of air (as measured by ppm O_s) was not considered a factor affecting fouling.

The linear relationship of S_o with processing time, as described in Fig. 11, may be the result of increased erosion of fouled material in the heat exchangers. The increased fouling demonstrated in Heater 1 (Fig. 2) does indicate that fouling rate is greater than erosion rate. However, the erosion rate is in all likelihood increasing along with the deposition rate in the heat exchanger. After approximately 40 min, Heater 2 demonstrated asymptotic fouling. Only lowfat milk deviates from this pattern. Due to the asymptotic fouling behavior in Heater 2, it appears that the positive slope of Fig. 11 is controlled to a great extent by the fouling of Heater 1.

Assuming no sediment exists at zero days storage, the fact that S_o was not zero implies that sediment falls out at a faster rate immediately after processing and packaging, than after six days when the sedimentation rate becomes constant. This observation is consistent with the sedimentation study of Ramsey (1982) who reported two rate periods. Sedimentation of eroded material may cause the high initial settling rate. The sedimentation rate after 6 days is slower and is affected by storage temperature. This may be evidence of particles forming during storage which settle out.

To characterize sedimentation during extended storage as a physical diffusion type settling process or a particle forming chemical reaction followed by settling of these particles, calculated diffusion coefficients and observed sedimentation rates were compared.

Average diffusion coefficients were calculated using the Stokes-Einstein equation for large molecules diffusing through a fluid of smaller molecules (Taylor 1938). The Stokes-Einstein equation is shown as:

$$D = \frac{kT_a}{6\pi r_h \eta} \tag{5}$$

The hydraulic radii (r_h) of the particles were assumed to be 1×10^{-7} m which is the approximate hydraulic radius of albumin, globulin and calcium caseinate (Rogers 1935). Viscosity (η) was evaluated at three temperatures using existing data (Swartzel 1982). The diffusion coefficients at temperatures of 4, 23, and 35°C were 6.54×10^{-9}, 8.16×10^{-9} and 1.09×10^{-8} m^2/h, respectively.

The apparent activation energies for diffusion rate and sedimentation rates were calculated using the Arrhenius equation (Levenspiel 1962).

The apparent activation energy (E_a) for diffusion using calculated diffusion coefficients was 11,200 J (2.68 kcal) which compares favorably with apparent activation energies for other diffusion processes (Taylor 1938). The E_a value for Srate was calculated to be 36,000 J (8.74 kcal) using the mean Srate estimates given in Fig. 12.

The E_a value for Srate was higher than expected if sedimentation in the carton during storage was only governed by diffusion. This indicates that some chemical reaction, resulting in increased sedimentation, may be occurring in the package.

Fat globules could tend to support potential sedimental materials due to attachment. However, this attachment effect seems minimized since differences in Srate could not be detected with respect to fat level.

The increased thermal treatment due to increasing the holding time did not affect Srate. Therefore, the potential for increased constituent transformation occurring in the holding tube apparently does not result in the later appearance of any appreciable sedimentable materials. The increased Srate due to increased thermal treatment as reported by Swartzel (1983b) is concerned more with increased thermal treatment in the heating sections. Increased exposure of product to a heat exchange surface increases both fouling and erosion, leading to increased potential for sediment.

Areas for future research include composition of sediment as well as composition, thermal conductivity, and distribution of fouled material in the heat exchanger. Chemical reactions occurring during processing and storage associated with fouling and sediment also require further investigation.

ACKNOWLEDGMENT

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NOMENCLATURE

Symbol	Quality Represented	Units
D	Diffussion coefficient	m^2/n
E_a	Activation Energy	J
gsed	Amount of sediment	g
k	Boltzmann's constant	J/°K
r_h	Hydraulic radius	m
R_1, R_2	Fouling resistance in Heater 1 and Heater 2, respectively	$\frac{m^2\ °C}{W}$
S_o	Intercept of linear model for gsed = f (storage time), also grams of sediment at 6 days storage	g
Srate	Sedimentation rate during storage	g/day
t_h	Mean residence time in the holding tube	s
t_p	Process time into run; may refer to time into run when product was packaged.	min
t_s	Storage time	days
T_a	Absolute temperature	°K
T_s	Storage temperature	°C
T_1, T_2, T_3, T_4, T_5	Process temperature	°C
U	Overall heat transfer coefficient	W/m^2C
U_o	Initial overall heat transfer	W/m^2C
η	Viscosity	Pa.s
ρ	Density of milk	kg/m^3

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FEASIBILITY OF SULFITE-MEDIATED β-CAROTENE DESTRUCTION IN HETEROGENEOUS SYSTEMS AND CARROTS

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ABSTRACT

The possible destruction of β-carotene during the oxidation of sulfur (IV) oxospecies in heterogeneous systems as well as carrots was investigated. The results showed that unlike similar reactions earlier reported in homogeneous systems, the oxidation of sulfur (IV) had no significant oxidative effect under these conditions. This was attributed to minimal interaction between the aqueous medium containing sulfur (IV) oxoanions and the carotenoid.

INTRODUCTION

Sulfur (IV) oxospecies (SO_2, HSO_3^-, SO_3^{2-}), are known to act as inhibitors of several oxidative processes in foods (Schroeter 1966). Some recent reports (Inoue and Hayatsu 1971; Inoue *et al.* 1980; Lamikanra 1982; Lizada and Yang 1981; Peiser and Yang 1979) however, have suggested that contrary to this long standing view, sulfur (IV) oxospecies are capable of interacting with food components such as β-carotene, amino and fatty acids, and hormones in an oxidative manner. In most of the reactions reported, investigations were carried out using model systems in homogeneous solutions. The reactions were shown to proceed by way of free radical mechanisms involving sulfite ion free radicals, and they were often inhibited by radical scavengers such as tocopherols and butylated hydroxy toluene (Peiser and Yang 1979). The products formed during the sulfite induced oxidation of β-carotene were recently characterized (Wedzicha and Lamikanra 1983), and this showed that highly oxygenated compounds, with little or no fragmentation or polymerization, containing 10 to 15 oxygen atoms per β-carotene molecule were formed.

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The ability of sulfur (IV) oxospecies to inhibit the oxidative deterioration of carotenoids in carrots, especially when added along with some antioxidants is well known (Arya *et al.* 1982). It therefore appears as if, for some reason, the sulfite induced oxidation of nutrients such as β-carotene do not take place in plant tissues. It was therefore necessary to investigate the possible reasons for the apparent reversed effect of sulfur (IV) oxospecies in carrots.

MATERIALS AND METHODS

Blanching of Carrots in Sulfite Solutions

For the preparation of dehydrated carrot, the sulfur (IV) oxoanions were added to the vegetable in the form of sodium hydrogen sulfite in the water used for blanching. A set of experiments was devised in which carrots were blanched in a medium in which sulfur (IV) oxoanions will normally be oxidized, the oxidation being induced by the addition of manganous ion. Thus, carrot slices (2mm thick) were blanched at boiling point in sodium acetate buffer (pH 5.6, 0.1M), containing sodium hydrogen sulfite (4.2-150 mM), with the corresponding controls in the absence of the additive. Manganous chloride concentrations in the solutions ranged between 0.005 to 2.5 mM. The reactions reported in the homogeneous systems showed that β-carotene pigments are rapidly and quantitatively destroyed in the presence of sulfur (IV) oxoanions (Peiser and Yang 1979; Wedzicha and Lamikanra 1983), hence similar reactions in the carrot samples should lead to discoloration of these vegetables. Loss of β-carotene in the carrot slices was therefore evaluated visually by comparing blanched fresh and freeze-dried carrots in the presence of sulfur (IV) oxoanions with those that were blanched in the absence of sulfur (IV). Sulfur (IV) oxoanion concentrations were determined using 5,5′-dithiobix (2-nitrobenzoic acid) (DTNB) (Humphrey *et al.* 1970). β-carotene pigments in the blanched fresh and freeze-dried carrots in the presence of sulfur (IV) oxoanions was observed after drying in a stream of hot air at 60°C to a moisture content of 12%.

Sulfur (IV) Oxoanion Destruction of β-Carotene Extracted with Chloroform, Hexane and Water from Carrots

Chloroform and hexane (250 ml of each) were used to exhaustively extract separate portions of freeze-dried carrots (20 g). The extracts were filtered and solvents removed, under reduced pressure at 25°C. It was demonstrated by ultra-violet and visible absorption profiles (Fig. 1), that β-carotene was the predominant compound in these extracts. The dry

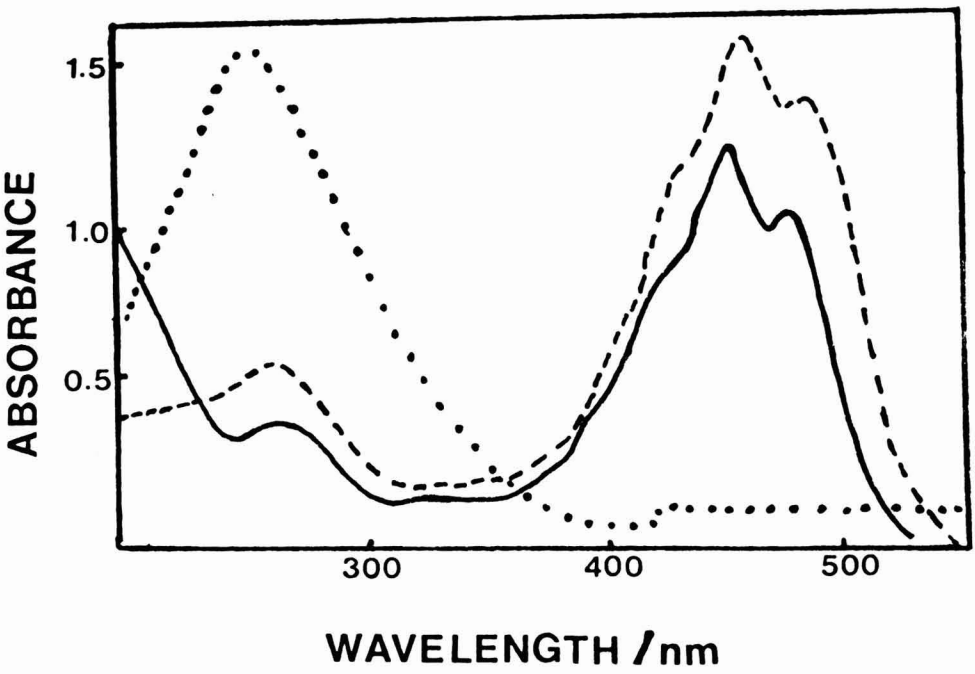

FIG. 1. ULTRA-VIOLET AND VISIBLE ABSORPTION SPECTRA OF (A) HEXANE EXTRACT FROM CARROTS (———), (B) CHLOROFORM EXTRACT FROM CARROTS (- - - - -), AND (C) THE PRODUCT OF A HETEROGENEOUS REACTION INVOLVING TWEEN STABILIZED β-CAROTENE AND SULFUR (IV) OXOANIONS IN AQUEOUS SOLUTION (· · · · ·)
In c, β-carotene was added in the form of a solution of the carotenoid (0.2% w/v) in chloroform.

extracts from chloroform and hexane fractions were each dissolved in chloroform, such that when this solution (180 μl) was added to a mixture of ethanol and water (3:1;10 ml) the absorbance at 454 nm was approximately 1.0. Manganous chloride (70 μM) and glycine (10 mM) were added to the solution to induce sulfur (IV) oxidation in these solutions. The presence of glycine for sulfur (IV) oxidation in ethanolic solutions has been demonstrated to be essential, since metal ions are incapable of catalyzing such reactions in this medium (Hayon *et al.* 1972; Schroeter 1966). To start the reaction, sodium hydrogen sulfite (0.5 ml; 1mM) was added to the mixture of buffered reactant (9.5 ml) in a 25 ml Erlenmeyer flask at 25°C. The progress of the reaction was followed by transferring the reaction mixture into a 1 cm silica cell, and the loss of β-carotene color was followed at 454 nm with the aid of a linear recorder. The control in this experiment involved a similar reaction in which synthesized β-carotene (7.9 μM) was used instead of the pigments extracted from carrots. The effect of water soluble extract from carrots on β-carotene loss

during sulfur (IV) oxoanion oxidation was investigated by the addition of a portion (100 μl) of the water extract (50 ml) from freeze-dried carrot slices (10 g) to similar reaction mixtures.

Heterogeneous Reactions of β-Carotene in Aqueous Solutions

β-carotene loss, as in the homogeneous reaction, was followed by measuring the change in absorbance of petroleum ether (bp 40-60°C) extracts of reaction mixtures. To carry out reactions, β-carotene was weighed into a blender and sodium acetate buffer (pH 5.6, 0.1 M; 250 ml) containing manganous chloride (1μM) was added. Sodium hydrogen sulfite (1.0 g) was dissolved in the solution and then blended for 2 min at 1-min intervals, for a total of 30 min to disperse the carotenoid. At the end of this period, the products were extracted and their visible and ultraviolet spectra recorded. In an attempt to aid the dispersion of β-carotene in aqueous solutions, various commercial emulsifiers were added to the solutions. The emulsifying agents used were Tween 80, Triton X 100 and Croda Sample "Datem." The concentrations of manganous chloride, emulsifying agents and sulfur (IV) oxoanions used were varied, one at a time, between 0.005 - 2.5 mM, 0.1 - 12.5% and 42 - 150 μM, respectively.

RESULTS AND DISCUSSION

The presence of sulfur (IV) oxoanions and manganous ions had no visible oxidative effect on β-carotene in dehydrated carrots derived from both balanced fresh and freeze-dried carrots. The experiments with freeze-dried carrots were carried out in order to improve the migration of water and the ions dissolved in it, into the structure of the vegetable. Sulfur (IV) oxoanions, measured using DTNB, were quantitatively oxidized in all of these experiments.

β-carotene, as it is present in nature is often associated with biological antioxidants such as tocopherols and ascorbic acid. The presence of these antioxidants in plant tissues may be argued to be responsible for the stability of these pigments when foods in which they are present are sulfited. In order to establish the extent to which these antioxidants influence β-carotene stability in biological systems in the presence of sulfur (IV) oxoradicals, homogeneous reactions similar to those earlier reported (Peiser and Yang 1979; Wedzicha and Lamikanra 1983) were carried out with hexane and chloroform extracts from freeze-dried carrots. The results showed a slower rate of β-carotene loss from the carrot extracts, when compared to the rate when synthesized β-carotene was used in a similar experiment (Table 1). However, these inhibitory effects were also found in the rate of sulfur (IV) oxoanion loss when this was

determined using DTNB. The addition of a portion of the water extract from freeze-dried carrots to the reaction mixture in which the synthesized carotenoid was used, caused a significant inhibitory effect in both β-carotene and sulfur (IV) oxidation. This was not unexpected, since the carbohydrates and ascorbic acid present in the aqueous extract have chain terminating properties on sulfur (IV) oxoanion oxidation. It therefore appears as if the effects of the antioxidant on β-carotene loss in these reactions resulted from the inhibitory effects on the rate of sulfur (IV) oxidation, which in turn retarded the rate of β-carotene loss. This, in effect, indicates that β-carotene will be oxidized, as long as sulfur (IV) oxidation takes place under these conditions.

Table 1. Effect of the Presence of Sulfur (IV) oxoanions, glycine, and manganous ions on β-carotene in ethanolic solutions consisting of the following after 30 s: (a) Pure β-carotene (b) Hexane extract from freeze-dried carrots (c) Chloroform extract from freeze-dried carrots and (d) a mixture of pure β-carotene and aqueous carrot extract. The corresponding sulfur (IV) levels, as measured using DTNB, are included for each experiment. Glycine was added to catalyze the oxidation of sulfur (IV) in ethanolic solution where metal ions alone are not capable of doing this.

	Initial Absorbance	Final Absorbance
[a]Pure β-carotene/A454	1.00	0.20
Sulfur (IV)/A412	0.50	0.02
[b]Hexane extract from carrots/A454	0.97	0.45
Sulfur (IV)/A412	0.50	0.16
[c]Chloroform extract from carrots/A454	0.93	0.42
Sulfur (IV)/A412	0.50	0.10
[d]Pure β-carotene and aqueous carrot extract/A454	1.01	0.69
Sulfur (IV)/A412	0.50	0.25

In order to study a system that is more closely related to food situations than those carried out in homogeneous mixtures, the feasibility of these reactions was investigated in heterogeneous systems. The results of experiments in which β-carotene was dispersed in aqueous solutions during sulfur (IV) oxidation showed no significant loss of β-carotene, despite the loss of sulfur (IV) during the reactions. The addition of commercial emulsifiers was also found to be ineffective in creating suitable

conditions for the oxidation of β-carotene in the presence of sulfur (IV) oxoradicals. When β-carotene was dissolved in chloroform (0.2% w/v) and this was added to Tween 80 prior to dispersing this mixture in aqueous solution (0.1% v/v), however, the bright yellow color of the emulsion was completely lost within 5 min, when sodium hydrogen sulfite was added. The chloroform extract showed no absorption due to β-carotene (Fig. 1). This result could not be reproduced when chloroform was used in the absence of the emulsifier.

It is evident from these results that for β-carotene to be oxodized during the oxidation of sulfur (IV) oxoanions in heterogeneous and food systems, a very fine dispersion of the pigments in an emulsion is essential. This is supported by the need to solubilize β-carotene with chloroform prior to the addition of an emulsifying agent in order that β-carotene oxidation would take place in the presence of sulfur (IV) oxoanions. However, in most foods, as is the case in carrots, β-carotene occurs in the crystalline form, and is present in definite chromoplasts. Under such conditions, interactions between carotenoid and the aqueous medium containing the additive is minimal, and the oxidation of carotenoids as a result of the presence of sulfur (IV) oxoradicals is not likely to take place to any significant extent.

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RESEARCH NOTE

A COMPARISON OF THE EFFECT OF OIL VERSUS PLASTICIZED VEGETABLE SHORTENING ON RATES OF GLUCOSE UTILIZATION IN NONENZYMATIC BROWNING

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ABSTRACT

Browning, as measured by the loss of glucose in a model system consisting of glucose, glutamate and starch, generally proceeded at a faster rate in the presence of lipids. The study examined the rates of glucose utilization over the temperature range of 25-55°C and at water activities (a_w) of 0.41 and 0.81. At the lower a_w the presence of lipids greatly accelerated the rate of glucose utilization; whereas, at the higher a_w the effect of the presence of lipids was minimized in relation to the effect of water. In addition, the presence of liquid oil tended to result in rates of glucose utilization that were faster than those observed with plasticized shortening, particularly at the lower a_w. The effect of lipids was to act as a mobile phase reducing the activation energy for the reaction.

INTRODUCTION

Nonenzymatic browning which utilizes glucose in the Maillard reaction can be a major deterioratie reaction in dry and intermediate moisture foods. Foods undergoing nonenzymatic browning usually exhibit a brown discoloration, as well as off-flavors and odors, loss of nutritional value and possibly undesirable textural changes.

It has been shown that the rate of browning is related to the state of the water in the system and that there is a maximum in rate at some intermediate water activity (a_w) usually around 0.6-0.8 (Lea and Hannan

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1947; Hendel *et al.* 1955; Sharp 1957; Loncin *et al.* 1968; Eichner and Karel 1972; Wolfram *et al.* 1974; Potthast *et al.* 1976; Labuza and Saltmarch 1981).

The antioxidative effect of Maillard reaction intermediates and reaction products on lipid oxidation has also been well documented (Tannenbaum *et al.* 1969; Eichner 1981; Lingnert and Erickson 1981; Lingnert and Waller 1983). Pokorny (1981) has presented a review of browning as a result of lipid protein interactions. Less is known about the direct effect of the presence of fats and oils on the rate of nonenzymatic browning. Studies by Pokorny *et al.* (1974) and Tannenbaum *et al.* (1969) have suggested that the browning of casein is accelerated in the presence of oils. Wolf *et al.* (1981) showed that the presence of oil might increase the rate of lysine loss in a model system. However, the direct effect of the presence of lipids on the kinetics of non-enzymatic browning, particularly the Maillard reaction, has not been clearly documented. In addition, the effect of the lipid physical state on nonenzymatic browning is unclear.

The specific objectives of this research were: (1) to determine on a kinetic basis, the effect of the presence of lipids on glucose utilization in nonenzymatic browning of a model system; and (2) to examine the kinetic effect of the physical state of the lipid, namely a liquid oil versus a semi-solid plasticized shortening, on the rate of glucose utilization.

MATERIALS AND METHODS

The model system used in this study was composed of glucose and monosodium glutamate (MSG) in equal molar quantities of 10% (wt) and 11.8% (wt), respectively, with corn starch as the inert portion of the system. The three test systems then contained either no lipid (control), 8.0% oil, or 8.0% plasticized shortening.

The liquid oil was Durkex 500 (Durkee Company, Cleveland, OH) while the plasticized shortening was a custom blended product made for General Mills. Both were mixtures of partially hydrogenated soybean and cottonseed oils. The liquid oil had an estimated AOM stability of 350 h versus 100 h for the shortening (Durkee Technical Information). Neither contained any antioxidants. The reported SFI (solid fat index) of the oil was zero (i.e., no solid) at all temperatures while the shortening had an SFI of 20, 12 and zero at 25, 35 and 45°C, respectively (General Mills). The oil had an apparent viscosity of 52 cp while the blended shortening was 70 cp both at 100°F.

The test system was prepared by thoroughly mixing the dry components and then, as appropriate, mixing with the oil or shortening. Each of the mixes was then passed through a laboratory homogenizer to reduce to

uniform particle size. Each of the three test systems was then humidified by adsorption to two different a_w's of 0.41 and 0.81 (about seven days for equilibration). These a_w's correspond to moisture contents of 9.3 and 25.8%, respectively, on a dry (fat-free) basis for all three systems. The monolayer value for cornstarch is about 7% on a dry basis. Portions of each test system were vacuum packed into 5 x 7 in., retort pouches, then stored for up to 270 days at constant temperatures of 25, 35, 45 and 55°C. The extent of the browning reaction was determined by measuring glucose utilization using reverse-phase high pressure liquid chromatography (DeVries *et al.* 1979). From three to five samples in duplicate were measured over the test period.

RESULTS AND DISCUSSION

The browning reaction between MSG and glucose was visually evident in all three test systems at all temperatures but was not measured because of the difficulty of extracting the pigment from the lipid phase. The rates of glucose loss were found to follow first order kinetics (ln glucose versus time) as shown in Fig. 1 for the oil system at 0.81 a_w. Other investigators such as Warmbier *et al.* (1976) and Labuza and Saltmarch (1981), have also observed first order kinetics for nonenzymatic browning when substrate loss was measured. Zero order rates for nonenzymatic browning have frequently been cited in the literature; however, these studies generally measure end product or pigment accumulation.

Table 1 presents the rate constants calculated by linear regression for each of the test conditions. At 0.41 a_w, the oil and shortening systems showed higher rate constants than the control. The oil system showed a rate constant for glucose loss from two to four times that of the control system. This difference was visually observed at the time of sampling with the oil sample exhibiting the greater degree of browning versus the shortening system which was only slightly darker than the control. The lower k for the shortening at 55°C (where SFI = 0) could be due to viscosity effects.

As would be expected, the rates of glucose utilization at 0.81 a_w were significantly greater than at 0.41 a_w. However, as seen in Table 1, the rate constants for the three test systems at 0.81 a_w are nearly identical. The visual differences observed at 0.41 a_w were also not apparent at 0.81 a_ww. There did not seem to be any direct correlation between SFI and the rate constants.

The energies of activation are also presented in Table 1. As seen, the major effect on the rate constant is an increase in a_w which decreases the activation energy by >50% at an a_w of 0.81 versus 0.41. The higher a_w

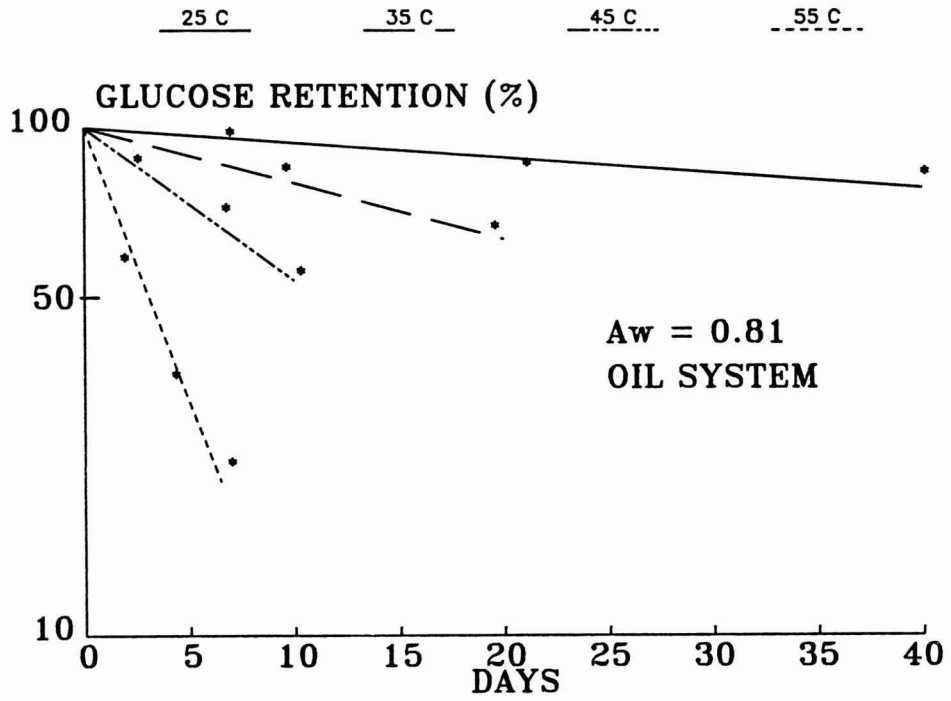

FIG. 1. FIRST ORDER PLOT OF LOW GLUCOSE REMAINING VERSUS TIME FOR THE OIL BASED MODEL SYSTEM AT 0.81 a_w

Table 1. Kinetic data for glucose utilization in model systems

		Rate Constant ($k(day^{-1})$) x 10^3				
a_w	Sample	25°C	35°C	45°C	55°C	E_A(kcal/mole)
0.41	Control	--	0.07	0.65	11.7	50.9
	Oil	--	0.32	1.00	24.3	40.6
	Shortening	--	0.19	0.91	13.8	42.7
0.81	Control	7.4	32.0	100.7	207.5	21.5
	Oil	8.7	34.1	100.6	223.7	20.9
	Shortening	8.7	33.9	104.8	214.2	20.7

illustrates that the greater amount of water present allows greater mobility and thus that the energy barrier for reaction (i.e., the activation energy of E_A) is decreased (Duckworth 1981). At 0.41 a_w, the presence of lipid also reduces the E_A, but the effect is only about 20%, suggesting that the lipid phase does not allow as great a mobility of the reactants (glucose and glutamate). At the high a_w the effect of the lipid phase is minimized, since enough water is present to allow maximum solubility and mobility.

These results suggest that at lower a_w's, nearer to the monolayer, both shortening and oil may provide a pseudo-liquid phase for mobilization of reactants that could lead to food deterioration. A similar effect has been noted by Naesens *et al.* (1982) with enzymatic activity in which the diffusion and mobility of reactants in low moisture systems is enhanced in the presence of lipophilic liquid phases. The practical significance of this study applies directly to dry mix products such as casseroles or gravy mixes which generally contain added fat for end product quality or anti-dusting characteristics. This study suggests that a decrease in shelf-life may result due to nonenzymatic browning between sugars and flavors such as MSG and hydrolyzed vegetable protein in the presence of fats or oils, whereby these lipids act as a solvent phase at low a_w's.

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

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Table 1. Activity of potato acyl-hydrolases on neutral lipids, galactolipids, and phospholipids

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Short notes will be published where the information is deemed sufficiently important to warrant rapid publication. The format for short papers may be similar to that for regular papers but more concisely written. Short notes may be of a less general nature and written principally for specialists in the particular area with which the manuscript is dealing. Manuscripts which do not meet the requirement of importance and necessity for rapid publication will, after notification of the author(s), be treated as regular papers. Regular papers may be very short.

Standard nomenclature as used in the scientific literature should be followed. Avoid laboratory jargon. If abbreviations or trade names are used, define the material or compound the first time that it is mentioned.

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