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CONTENTS

RELATION BETWEEN MECHANICAL PROPERTIES OF APPLE FRUIT AND SENSORY QUALITY

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ABSTRACT

In order to select those parameters determining the apple fruit acceptability for the consumer, fruit texture was measured using several methods. Three methods were selected to do tests on Golden Delicious apples with differing acceptability for the consumer. The three methods used were an uniaxial compression test on cylindrical fruit samples, a resonance test on cylindrical apple specimen, and a non-destructive dynamic test.

Most useful information is given in the dynamic tests. The apparent elastic modulus derived from the destructive dynamic test and the stiffness factor ($S = f^2m^{2/3}$) *as well as the damping ratio at the spheroidal vibration mode of a whole apple derived from nondestructive dynamic tests seem to be parameters correlating highly with the apple fruit acceptability, hence with the internal quality, for the consumer.*

INTRODUCTION

Fruit texture is an important parameter for the quality criteria on which the consumers' acceptance is based. Research seems to focus on using some changes in mechanical properties to indicate changes in fruit texture (Mohsenin 1970; Tijskens 1979). These mechanical properties can be measured either in a destructive or a nondestructive way, in quasi-static or dynamic experiments.

Dynamic resonant behavior in the audio-frequency range was investigated by several authors as a means for the nondestructive testing of fruit firmness. From the transmission curve of acoustical waves through the apple, the second resonant frequency seemed to be a good measure of fruit firmness (Abbott *et al.* 1968a,b; Finney 1970). Yong and Bilanski (1979) claimed this second resonant frequency to correspond with the spheroidal mode of vibration of the apple. For the experimental set-up used by Finney (1970) this is affirmed by Van Woensel

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and De Baerdemaeker (1985). The second resonant frequency measured with the set-up used by Abbott *et al.* was associated with the second spheroidal mode.

Cooke and Rand (1973) calculated that the quantity $f^2m^{2/3}$, with f the resonant frequency at the first spheroidal mode and m the apple mass, would be a measure for the elastic moduli of the fruit.

The stiffness factor f^2m was used by Abbott *et al.* (1968a,b) and Finney (1970). Abbott *et al.* found this stiffness factor to decrease with the later date of fruit harvesting and after severely bruising the fruit. Finney observed that this stiffness factor decreases with storage time, and that it correlates highly with the elastic modulus of the fruit flesh and with Magness-Taylor forces.

In doing nondestructive dynamic tests on apples, Yamamoto *et al.* (1980) found the second resonant frequency f and the factor f^2m to correlate to the Magness-Taylor tests and to sensory measurements, but the latter only for Golden Starking apples and not for Golden Delicious apples.

Van Woensel and De Baerdemaeker (1983) found that the stiffness factor $f^2m^{2/3}$, as defined by Cooke (1972), showed a sharp decline at the storage time when the fruit reached its climacteric maximum (i.e. the period of highest metabolic activity in which the fruit reaches optimal maturity and after which the strict senescence period starts) as determined by the activity of the apple fruit malic enzyme. (These results were obtained from measurements on Golden Delicious apples and Red Boskoop apples.). Hence, this stiffness factor seems to be a useful parameter to determine sensory quality of the fruit.

Resonant frequencies of cylindrical apple specimen can be used to calculate the apparent elastic modulus, the shear modulus and the associated loss moduli, which are a measure for internal damping (McLachlan 1951). Based on this kind of dynamic measurements with cylindrical samples, Finney (1967) found values for the apparent elastic modulus which were higher than those obtained from uniaxial compression tests.

From uniaxial compression tests on cylindrical apple samples, Diehl and Hamann (1979) found the stress to failure to be a significant indicator for apple texture, being a predictor of crispness and mastication release. They also corroborate the assertion of Segerlind and Dal Fabbro (1978) that the apple flesh fails when this stress exceeds a critical value. Applying several texture measuring methods, a series of quasi-static methods, Tijskens (1979) concluded that the most useful information is given by the breaking force during compression of cylindrical samples of apple tissue, but he mentioned that hardness and firmness cannot provide useful information about the internal quality of apples at the time they loose their acceptability for the consumer.

Most of previous research has been centered on deriving fruit texture from measuring mechanical properties in different ways. At the present time there is still a need for a physical testing method that can give sufficient information about the internal textural quality of the fruit and the acceptability for the consumer.

The objectives of this study were: (1) to evaluate various static and dynamic testing methods for obtaining parameters which may relate to fruit texture. (2) to investigate the consistency of the obtained parameters for the texture information as related to the fruit acceptability for the consumer.

The work reported here is based on the results from experiments carried out on eight groups of Golden Delicious apples at different maturity stages and with different acceptability for the consumer. These differences were obtained by different storage conditions.

TABLE 1.
DESCRIPTION OF THE ACCEPTABILITY GROUPS

Acceptability group number	Description : color (chart color)	Comment
1	green (5)	unripe and hard
2	green (6)	unripe and hard
3	green to yellow (7)	slightly unripe
4	yellow (8)	ripe, crisp and juicy (attractive)
5	yellow (8)	ripe, crisp and juicy (attractive)
6	yellow (8)	slightly wrinkled and soft
7	yellow (8)	wrinkled, soft and mealy
8	yellow (8), brown wrinkles	strongly wrinkled, very soft, and very mealy

MATERIALS AND METHODS

The composition of the acceptability groups was partially based upon the apple color and partially on their appearance and subjective firmness appreciation. A commercial ‘color chart’ was used, scaled from 1 (dark green) to 8 (yellow, ripe). Subjective firmness evaluation was done by 3 independent judges and was based on squeezing a fruit in the hand and also making a few bites. The groups are described in Table 1.

From each group five apples (with a diameter over 70 mm) were subjective first to a nondestructive test, using a technique as developed by Finney (1967).

Thereafter three cylindrical samples (with a height of 18 mm and a diameter of 18 mm) were cut from these apples, and subjected to a vibration test. Finally another set of 6 cylindrical samples (with a height of 11 mm and a diameter of 11 mm) was subjected to an uniaxial compression test, as used by Segerlind and Dal Fabbro (1978).

MEASURING TECHNIQUES

Nondesctructive Resonance Test

The sonic technique developed by Finney (1967) was used. The apple is placed on a force transducer, mounted on a vibrating exciter (B & K 4808). The exciter is driven by a pseudo-random noise signal with a bandwidth of 1600 Hz. A low mass accelerometer (2.4 g) is placed on the opposite side of the apple, in the same direction as the load cell (Fig. 1).

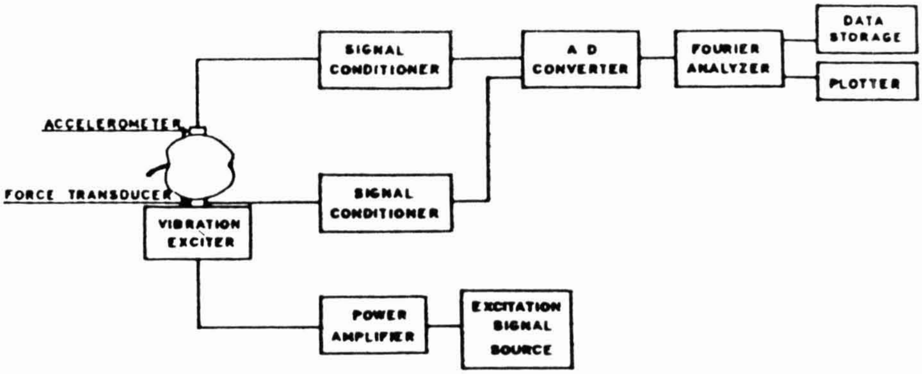

FIG. 1. MEASUREMENT SET-UP FOR THE FRUIT RESONANCE TEST

A structural dynamics analyser (HP 5423 A) calculates the transfer function of the acoustical waves as the ratio of the Fourier Transform of the accelerometer signal to the Fourier Transform of the force signal (Fig. 2).

As asserted by Yong and Bilanski (1979) and measured by Van Woensel and De Baerdemaeker (1985) the second resonant frequency can be considered as belonging to the first spheroidal mode, shown in Fig. 3.

According to the theory developed by Cooke (1972), from this second resonant frequency, f, a stiffness factor S can be calculated as $S = f^2m^{2/3}$ (1), with m the apple mass. This stiffness factor was shown to be independent of fruit size.

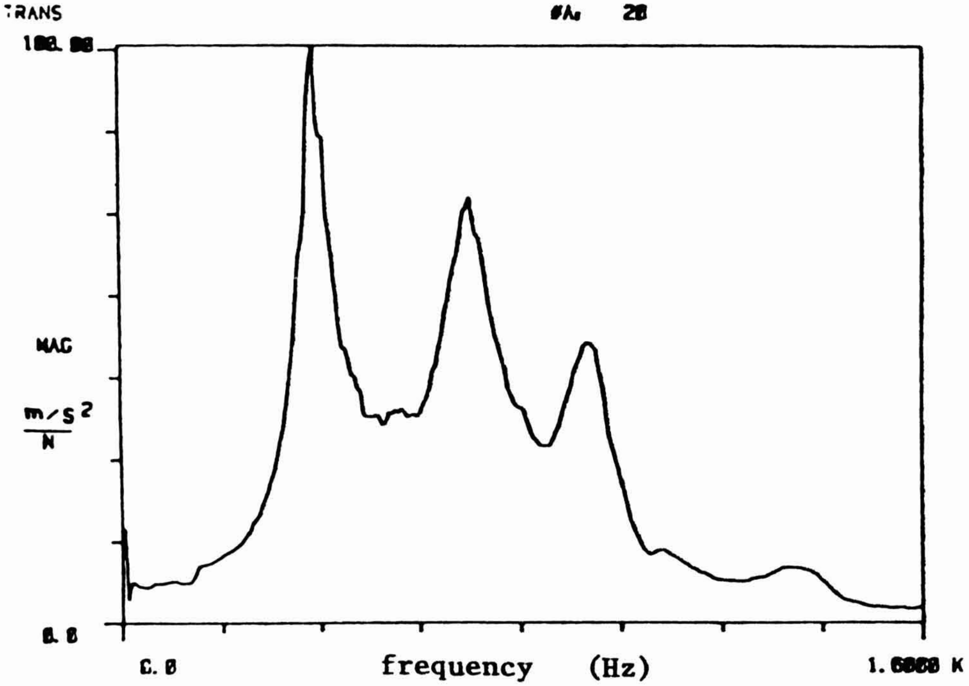

FIG. 2. TYPICAL FRUIT FREQUENCY RESPONSE CURVE

Using the 3-media elastic sphere model developed by Cooke and Rand (1973) shear and apparent elastic modulus can be calculated from this stiffness factor. In this model the apple core is treated as a sphere consisting of a homogeneous material. Cooke (1972) stated that the apple flesh shear modulus G_C can be calculated as

$$G_C = S\rho^{1/3} R_C, \tag{2}$$

where ρ is the apple flesh mass density and R_C is a dimensionless conversion ratio. This conversion ratio R_C is explicitely dependent on the radii and density ratios of the apple skin, the apple flesh, and the core, hence dependent on the kind of the fruit. For the spheroidal mode of vibration, the conversion factor R_C is nearly independent of the flesh to skin ratios, but R_C is more influenced by the core charcteristics. In a theoretical study Cooke (1972) estimated R_C as being in the range of 2.0 to 3.5. Based on Finney's data (1970), R_C was calculated to lie between 1.0 and 1.5 (for Red Delicious apples). The apple flesh mass density ρ

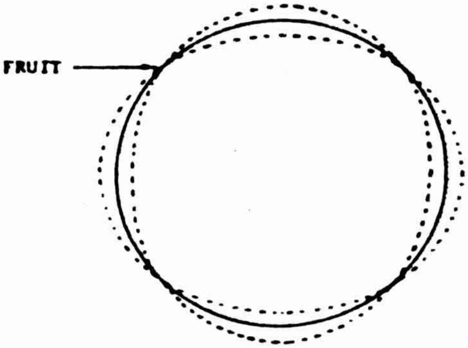

FIG. 3. FIRST SPHEROIDAL MODE OF VIBRATION AT SECOND RESONANT FREQUENCY (Yong & Bilanski 1979)

can be approximated as 0.84 g cm^{-3} (Mohsenin 1970). From this apple flesh shear modulus the apparent elastic modulus can be calculated as

$$E_c = G_c\,2\,(1 + \nu)$$
or
$$E_c = S\,\rho^{1/3}\,R_c\,2\,(1 + \nu), \tag{3}$$

with θ the Poisson ratio. For Golden Delicious apples this ratio can be estimated as 0.25 (Mohsenin 1970) and can be condsidered constant for the small deformation involved.

The loss moduli associated with Gc and Ec can be calculated as

$$G'_c = G_c\,2\,\xi_c \tag{4}$$
and
$$E'_c = E_c\,2\,\xi_c, \tag{5}$$

with ξc the damping ratio associated with the second resonant frequency.

Destructive Resonance Test

For this test a measurement set-up is used, which is quite similar to the one used for the nondestructive tests.

A cylindrical sample of apple tissue, with mass Ms, loaded with a mass M is placed on a force transducer, mounted on a vibrating exciter. The exciter is driven by a pseudo-random noise signal with a bandwidth of 400 Hz. Again a low mass accelerometer is placed on top of the system in the same direction as the load cell (Fig. 4).

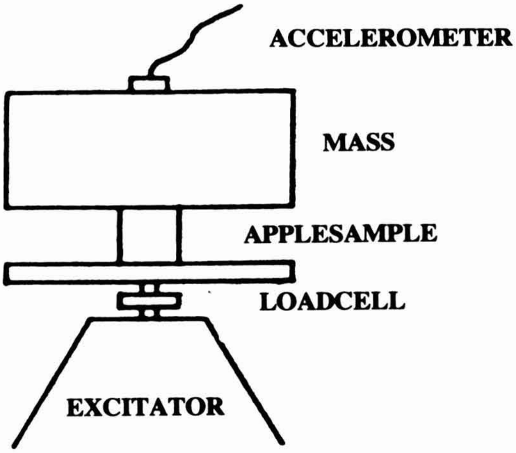

FIG. 4. MEASUREMENT SET-UP FOR THE DESTRUCTIVE DYNAMIC TEST

A simplified representation of this system is given by the lumped parameter system shown in Fig. 5. This is a configuration with a mass M, a spring with spring constant k, and a damper with damping constant c. The sample mass Ms can be ignored.

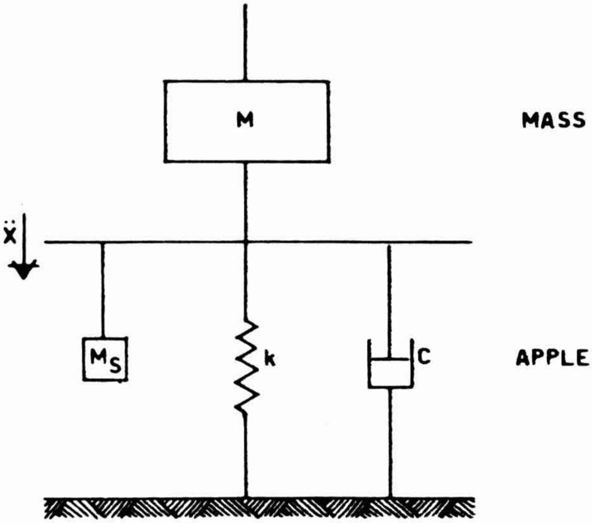

FIG. 5. LUMPED PARAMETER MODEL CORRESPONDING TO THE EXPERIMENTAL SET-UP SHOWN IN FIG. 4

When a force F(t) acts on this system, the dynamic equilibrium is described by the followed differential equation:

$$M x + c x + k x = F(t) \qquad (6)$$

Fourier transforming and manipulating this equation results in

$$\frac{X(\omega)}{F(\omega)} = \frac{-\omega^2/k}{1 - (\omega / \omega_n)^2 + 2j(\omega / \omega_n)} \qquad (7)$$

The ratio of the Fourier Transform of the accelerometer signal to the Fourier Transform of the force signal is calculated by the structural dynamics analyser. A direct transfer function is obtained as shown in Fig. 6.

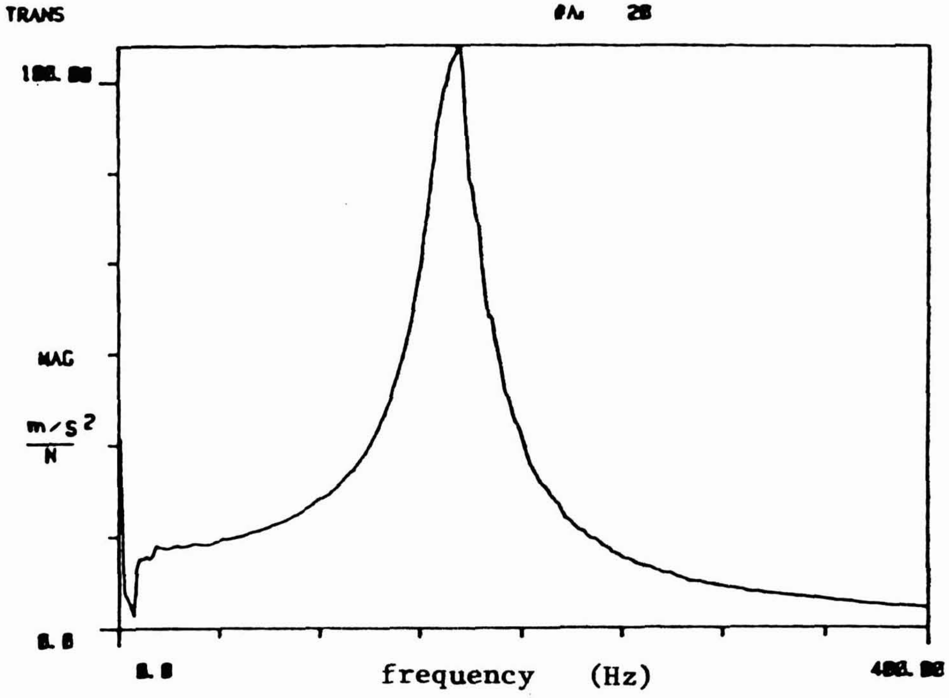

FIG. 6. ACCELERATION TRANSFER FUNCTION OF A VIBRATING CYLINDRICAL APPLE SAMPLE LOADED WITH A MASS

From this transfer function a value for the natural frequency fn of the vibrating system and the associated damping ratio ξ is derived.

From fn and ξ the spring constant k and the damping constant c can be calculated as

$$k = \omega_n^2 m, \text{ where } \omega_n = 2\Pi f_n, \qquad (8), (9)$$

and

$$c = \xi\, 2.(k.m)^{1/2} \qquad (10)$$

Finally, the apparent elastic modulus E and corresponding loss modulus E′ of the measured sample are formed by the equations:

$$E = k\, l/A \qquad (11)$$

and

$$E' = c\, \omega_n l/A, \qquad (12)$$

where l is the sample length and A is the cross section area of the apple specimen.

Uniaxial Compression Test

Cylindrical apple samples were taken out of a slice from the middle part of the apple. The samples were compressed with a displacement speed of 0.25 mm/s using a Wolpert universal testing machine. The force output was read by a microcomputer using an AD converter and the stress-strain curve was computed.

The apparent elastic modulus was determined from the middle third part of this curve, as illustrated in Fig. 7. This definition of a chord modulus (Mohsenin 1970) for bio-materials, and specifically for Golden Delicious apples, is proven to give consistent results between different research groups De Baerdemaeker *et al.* 1986.

RESULTS AND DISCUSSION

In Table 2 the matrix of (linear) correlation coefficients are given between the measured parameters in the different tests and the acceptability degree (given by the number of the acceptability group, as defined in Table 1, to which the apple belongs).

Relation Between Each of the Measured Mechanical Properties and the Apple Fruit Acceptability Group (Table 2)

Parameters Obtained in the Uniaxial Compression Test. From Table 2 it is

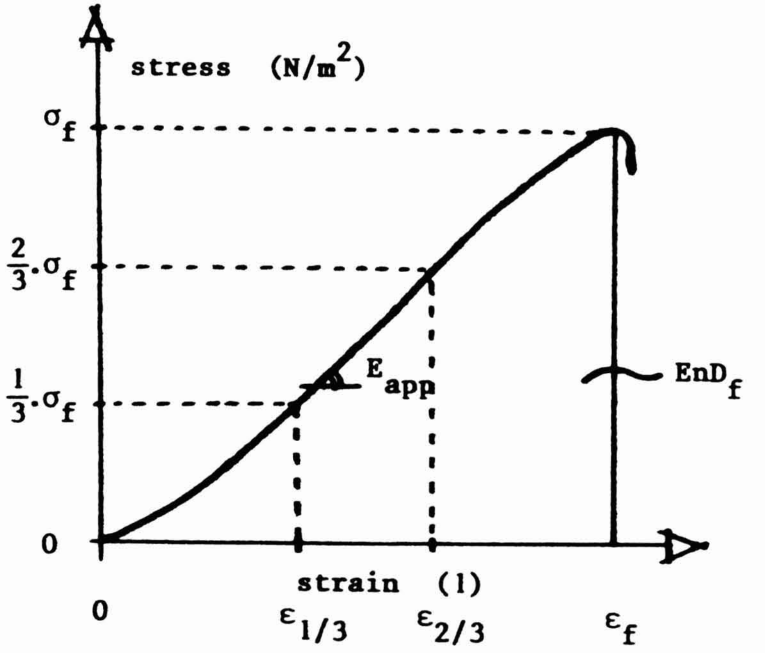

FIG. 7. STRESS-STRAIN CURVE DURING QUASI-STATIC COMPRESSION AND DERIVED MECHANICAL PROPERTIES

TABLE 2.
CORRELATION COEFFICIENTS BETWEEN ACCEPTABILITY DEGREE AND MECHANICAL PROPERTIES

	uniaxial compression test		destructive resonance test			non-destructive resonance test			
	σ_f	E_a	E_a	E'	ξ	f	S	S'	ξ_c
Group	-0.617	-0.562	-0.923	-0.904	0.290	-0.970	-0.979	-0.898	0.882

clear that neither the failure stress σ_f nor the apparent elastic modulus E_a are a good measure for the apple acceptability group.

Parameters Derived from the Destructive Resonance Test. There is no correlation between the damping factor ξ of the vibrating cylindrical apple samples and the apple acceptability group, but there is a high correlation for both the calculated apparent elastic modulus E_a and the corresponding loss modulus E′. E_a and E′ are plotted against the apple acceptability group in Fig. 8 and 9.

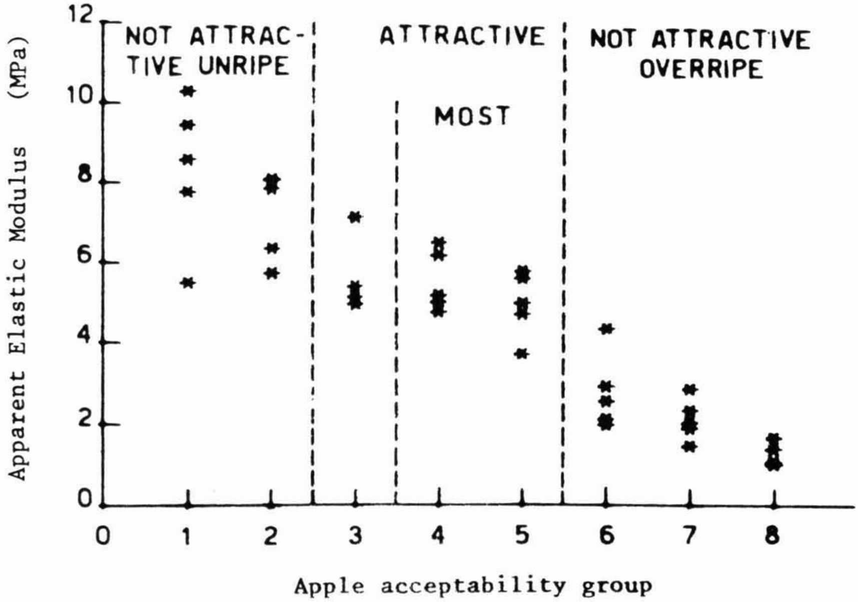

FIG. 8. APPARENT ELASTIC MODULUS (E_a) OBTAINED FROM DESTRUCTIVE RESONANCE TESTING VERSUS APPLE ACCEPTABILITY GROUP

Parameters Derived from Nondestructive Resonance Test. All of these parameters are highly correlated with the apple quality. The resonant frequency f at the spheroidal mode of vibration and the associated damping ratio ξ_c are plotted in Fig. 10 and 11. In Fig. 12 and 13 the stiffness factor S and corresponding loss factor S′ ($S' = 2\xi_c S$) are shown.

Relation Between the Texture Parameters Derived from the Diferent Kinds of Tests (Table 3)

From Table 3 there seems to be a high correlation between the apparent elastic modulus and associated loss modulus E′ derived from the destructive resonance test and all of the parameters derived from the nondestructive dynamic test.

A plot of apparent elastic modulus E_a versus stiffness coefficient S is shown in Fig. 14. There is a linear relationship between E and S with correlation coefficient $r = 0.918$. From this relationship R_c can be estimated using formula (2). Approximately as 0.84 g cm^{-3} and as 0.25 (Mohsenin 1970), the value of R_c is situated around 2.2. This value agrees well with the theoretically derived range for R_c from 2.0 to 3.5 (Van Woensel and De Baerdemaeker 1983).

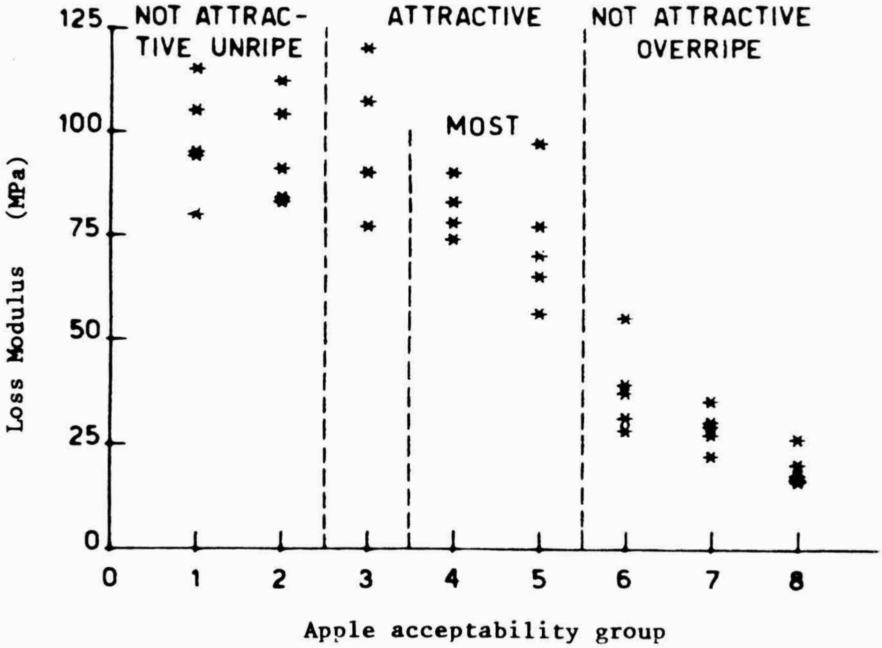

FIG. 9. LOSS MODULUS (E′′) DERIVED FROM THE DESTRUCTIVE VIBRATION TEST VERSUS APPLE ACCEPTABILITY GROUP

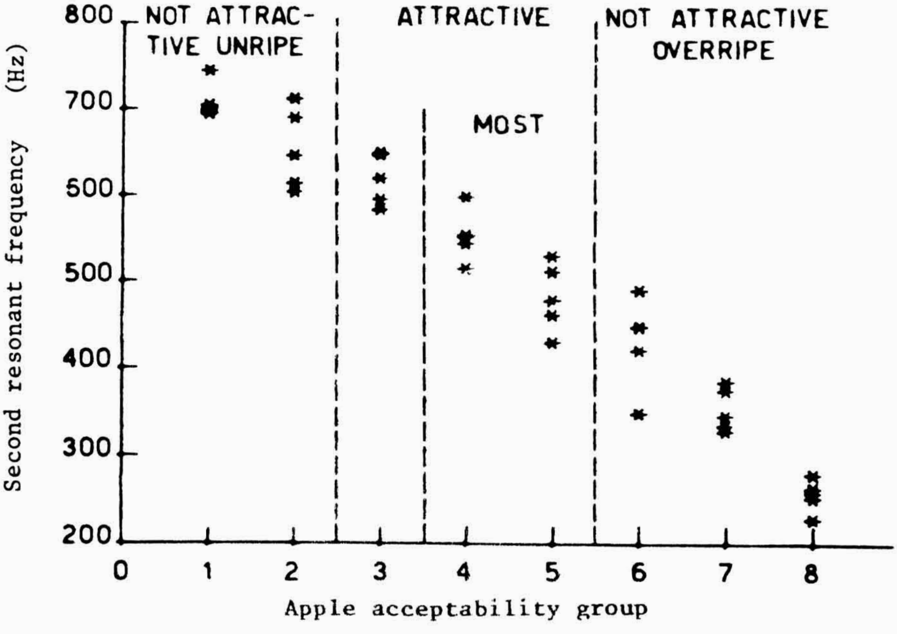

FIG. 10. SECOND RESONANT FREQUENCY OF A VIBRATING APPLE FRUIT VERSUS APPLE ACCEPTABILITY GROUP

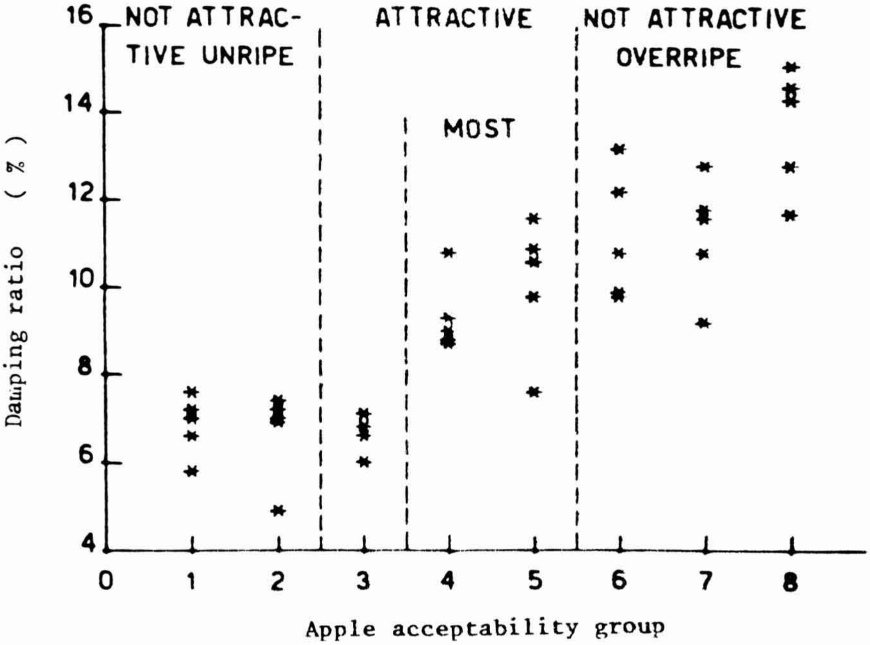

FIG. 11. THE DAMPING RATIO ξ_C, ASSOCIATED WITH THE APPLE RESONANT FREQUENCY AT THE FIRST SPHEROIDAL MODE, VERSUS THE APPLE ACCEPTABILITY GROUP

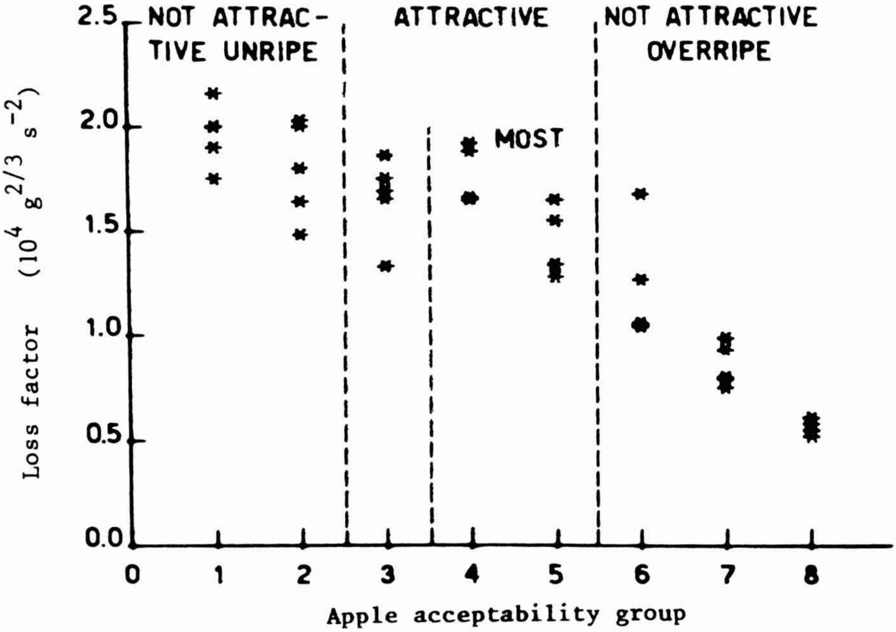

FIG. 12. THE STIFFNESS FACTOR S VERSUS APPLE ACCEPTABILITY GROUP

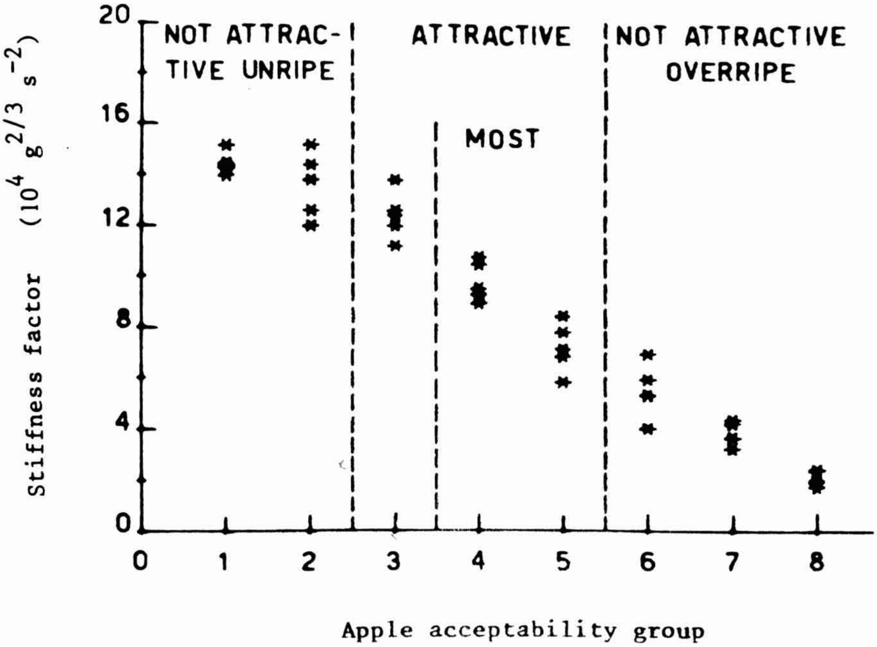

FIG. 13. THE LOSS FACTOR S′ VERSUS APPLE ACCEPTABILITY GROUP

TABLE 3.
CORRELATION MATRIX FOR ALL MEASURED PARAMETERS

	uniaxial compression test		destructive resonance test			non-destructive resonance test			
	σ_f	E_a	E_a	E'	ξ	f	S	S'	ξ_c
f	1.								
E_a	0.700	1.							
E_a	0.540	0.550	1.						
E'	0.638	0.682	0.947	1.					
	0.004	0.182	-0.414	-0.238	1.				
f	0.616	0.560	0.926	0.912	-0.282	1.			
S	0.651	0.571	0.918	0.921	-0.254	0.986	1.		
S'	0.654	0.634	0.893	0.904	-0.179	0.982	0.899	1.	
c	-0.549	-0.422	-0.783	-0.802	0.219	-0.912	-0.913	-0.728	1.

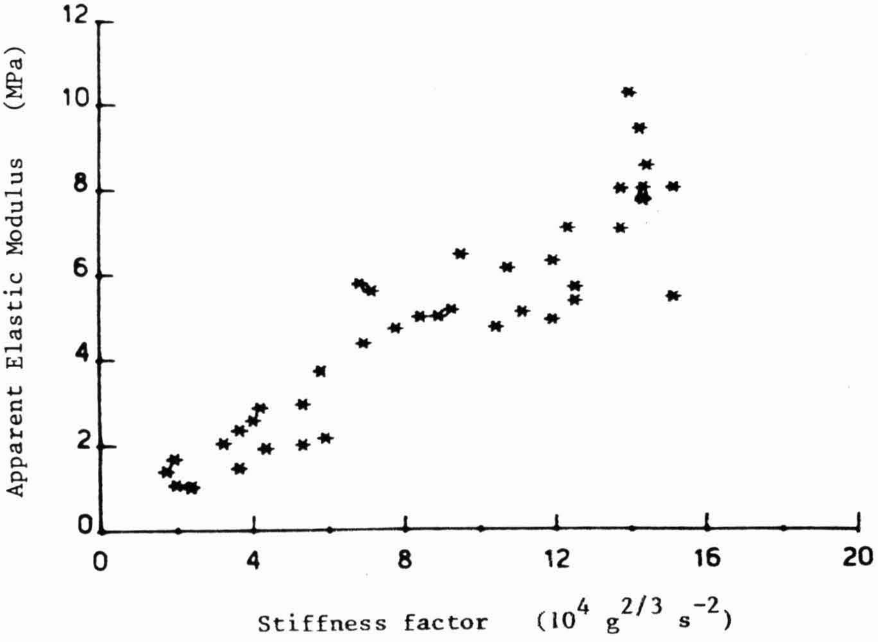

FIG. 14. RELATION BETWEEN THE APPARENT ELASTIC MODULUS E, OBTAINED IN A DESTRUCTIVE DYNAMIC TEST, AND THE STIFFNESS FACTOR S, DERIVED FROM NONDESTRUCTIVE DYNAMIC TESTING OF A WHOLE APPLE

The damping ratio ξ derived from the vibration tests on cylindrical samples correlates neither with the apple acceptability group nor with any other measured property. This damping ratio was expected to be a measure for the presence of free water between the parenchyma cells of the apple tissue. The amount of free water varies with the stage of maturity of the fruit. Probably this damping ratio is strongly influenced by the presence of a thin film of water between the apple sample and the loading mass or the vibrating plate. This moistening effect has been observed and is due to the cutting of the tissue. So it seems that the damping ratio from destructive dynamic tests does not give any information about the apple quality.

On the other hand the damping ratio ξ_c derived in the nondestructive test seems to be a good measure for the apple acceptability group (Fig. 11), and correlates highly with the mechanical characteristics as the dynamic apparent elastic modulus and corresponding loss modulus E′, as well as with the resonant frequency f and the stiffness factor S.

CONCLUSIONS

In this study static and dynamic tests were conducted to obtain parameters related to the texture of the apple fruit.

Two dynamic tests, a destructive one and a nondestructive one, can provide useful information about the sensory quality of apple fruits.

Vibration tests on cylindrical samples of apple tissue were used to derive the apparent elastic modulus E_a, which is a measure of fruit firmness.

Vibration tests on whole apples resulted in a stiffness factor S which is a measure of the shear modulus of the apple flesh, and a damping ratio ξ_c, which strongly depend on the maturity stage of the fruit.

All of these parameters (E_a, S and ξ_c) were more consistent indicators of the apple fruit acceptability than parameters obtained from static tests. The result indicates that these techniques may be useful for monitoring textural changes of fruit during storage and perhaps also for sorting purposes. It remains to be investigated how a combination of the two dynamic tests can further improve the observed relationships.

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MOISTURE EQUILIBRIA OF SOME DEHYDRATED CASSAVA AND YAM PRODUCTS

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ABSTRACT

The moisture content for optimum stability of the products made from cassava (gari and lafun) and yam (elubo and instant pounded yam flour) were calculated from equilibrium moisture data using the BET equation.

The sorption properties for products (lafun and elubo) that were not precooked prior to final drying were similar. The moisture content for optimum stability of the cassava and yam products lies between 6.5–8.0% under conditions that simulated distribution and marketing of the products.

Storage tests confirm that the calculated moisture values from the sorption isotherms indicate that aside from differences in the pretreatment conditions the poor keeping qualities of the products could be improved by further drying to moisture levels of 6.5–8.0% prior to packaging in moisture proof containers.

INTRODUCTION

Dehydrated products of cassava (gari and lafun) and yam (yam flour (elubo) and instant pounded yam flour are important carbohydrate foods in many parts of West Africa especially Nigeria. These products which are mostly produced by traditional and lately improved technologies, enjoy wide acceptability in many homes when reconstituted into local dishes. However, these products often deteriorate in quality because of an off-flavor and moldiness which they develop and make then unmarketable within a short period (8 weeks) of production. As typically manufactured, these products have a high moisture content 13–14% and are normally packaged in jute bags for the purpose of distribution and marketing, a condition that allows for free entry of water vapor and pest. Adesuyi (1973) has identified insect infestation and high moisture content of processed agricultural crops as the major cause of food losses in Nigeria.

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A knowledge of the moisture sorption of most dehydrated or formulated foods is important for predicting quality stability during storage and selection of packaging material for retail purposes (Makower and Dehority 1943; Gane 1950; Henderson 1952; Houston and Kester 1954; Taylor 1961; Labuza 1968). The moisture levels at which some dehydrated potato foods have good storage stability have been found to agree closely with the moisture levels calculated from the moisture sorption isotherms (Salwin 1959, 1963; Strolle and Cording 1965; Mazza 1982).

Using the Brunauer, Emmett and Teller theory of multimolecular adsorption, (Brunauer *et al.* 1938), the optimum moisture level for stability of potato flake was to be 5.1 to 5.8% (Drazga *et al.* 1964).

The moisture sorption properties of foods have been shown to be influenced by food composition (Makower and Dehority 1943; Burton 1949; Crapiste and Rostein 1982), processing treatment (Strolle and Cording 1965; Hellman and Melvin 1950; Mazza 1982) and temperature and relative humidity (Deobald 1964; Chen and Clayton 1971; Inglesias and Chirife 1976; Bruin *et al.* 1980).

Cassava and yam products are mainly obtained by the traditional processing techniques which involve mechanical disruption of the starch granules followed by dehydration. Lately however these processes have been improved and modified for high production by the adoption of mechanization. The mechanically produced gari, a granular cassava product, still contain a high moisture content as the traditionally prepared gari and it often develops an off-flavor unless it is sold within a few weeks.

The problem of poor keeping quality of many dehydrated foods in the tropics is related to their moisture uptake during merchandising because of poor packaging materials and the moisture levels at which they are prepared. Rodriquez-Soza, (1973) indicated that yam chips made from Lisbon yam needed special packaging for better shelf-life. Berry and Dickerson 1973; Quast and Teixera-Neto 1976 suggested that variations in the traditional processing operations and environmental conditions could affect the storage stability of many dehydrated foods in the tropics.

Presently there is not much information on the moisture sorption data of many African food products. Such information on the optimum moisture levels which should be arrived at during manufacture and for selection of good packaging material is necessary in order to avoid their quality deterioration.

In summary this study was made in order to (1) determine the moisture sorption characteristics to some products made from cassava and yam, (2) to calculate their optimum moisture level for storage stability (3) to compare the moisture levels with storage tests.

MATERIALS AND METHODS

Samples of cassava and yam products freshly made by local processors were used for this investigation:

The cassava products were:

(1) Gari - a granular food product prepared from peeled, grated, fermented cassava roots.

(2) Lafun - a raw sundried flour obtained by milling peeled cassava chips.

The yam products were:

(1) Yam-flour (elubo) - peeled, partially parboiled, sundried yam chips milled to flour.

(2) Instant pounded yam flour - a convenience new yam product developed in the Department of Food Science, University of Ife. The product was made by milling, peeled, diced, pregelled dried yams.

All the samples were passed through a sieve with an aperture of 350 micron. The moisture content of the product was determined by the vacuum oven method (AOAC 1980). All determinations were made in duplicate.

Determination of Equilibrium Moisture Content

A static gravimetric method of determining the equilibrium moisture content was adopted. Duplicate samples each of the cassava products (gari, lafun) and yam (yam flour (elubo) and instant pounded yam flour were weighed 10 g into dishes and placed on wire baskets in dessicators containing different levels of saturated salt solutions. The salt solutions were chosen in order to provide a range of relative humidities from 11–70%. Saturated solutions of the following salts: magnesium chloride, magnesium nitrate, ammomium sulfate, lithium chloride, sodium hydrogen phosphate and potassium sulfate were prepared and placed in separate dessicators in order to build up air corresponding to their relative humidities (Wink 1946 and Young 1967). The dessicators containing the samples were kept in incubators maintained at 25 °C or 32 °C. The samples were weighed periodically until they attained moisture equilibrium when four consecutive weighings showed no increase in weight. The equilibrium moisture content was calculated using the data of initial moisture content and the amount of moisture gained or lost until equilibration.

The equilibrium moisture content on dry weight basis was plotted against the equilibrium relative humidity to obtain the moisture isotherm. From this data, the sorption isotherm curve was obtained by employing the BET equation based on the theory of multimolecular adsorption as adopted by Strolle and Cording 1965). For most of the products moisture equilibrium was attained in 21 days and few samples which showed evidence of mold growth at high relative humidities were discarded and repeated.

Storage Tests and Sensory Evaluation

Freshly made products prepared for retail were dried to the moisture level corresponding to their calculated equilibrium moisture level of 4.5 to 5.0% (d.b) and then to moisture level of 7.5 ± 1.0% which is slightly higher than the monomolecular layer as determined by the BET equation (Brunauer *et al.* 1938). These moisture levels were used in order to test whether these new or calculated moisture levels would ensure their stability in comparison to the moisture levels normally associated with the freshly made samples which were used as control.

The samples containing different levels of moisture were kept in separate bottles and placed in incubators maintained at 25 °C or 32 °C for 4 months. These temperatures represent the range of temperatures that the products could encounter under normal marketing and distribution conditions in West Africa.

The products were assessed for changes in flavor in the dried forms or reconstituted forms at 30 day intervals by a taste panel procedure. Panelists were selected on the basis of their familiarity with the products and ability to distinguish off-flavor in the various forms of the products.

Panelists were asked to sniff-test the dried stored samples for the degree of off-flavor in comparison with the freshly made samples using a rank order test with 1 = unacceptable and dislike extremely due to off-flavor; 9 = acceptable like extremely. The fresh and stored products were also reconstituted with water, often with cooking, for comparison on the basis of flavor, taste and acceptability.

The reconstitution was done by adding 1 part of the product (fresh or stored) to 3 parts of water (96–98 °C), stirring with a paddle until a product similar to the traditionally prepared paste was obtained. The cassava and yam products are normally purchased in their dried forms but are prepared in the form of paste as described above in many West African homes.

RESULTS AND DISCUSSION

The equilibrium moisture content expressed on moisture free basis corresponding to each relative humidity and temperature for the cassava and yam products are presented in Table 1.

The data reveal that the products, elubo and lafun that had not been heat pretreated prior to drying had a higher equilibrium moisture values than the precooked or pregelatinized products (gari and instant pounded yam flour). These differences may be attributed to the physical changes of the starch particles in these products. The effect of physical changes and modification of starch properties on the moisture equilibrium value have been reported (Makower and Dehority 1943). For instance the equilibrium moisture content

TABLE 1.
EQUILIBRIUM MOISTURE CONTENT OF DEHYDRATED CASSAVA AND YAM PRODUCTS

Products	Temp. (°C)	Relative humidity						
		12.5	22.5	35.6	43.7	50.0	63.5	73.0
Cassava								
Gari	25	5.0	5.8	6.5	7.5	7.9	9.5	11.2
	32	4.5	5.1	6.2	6.2	7.7	9.1	10.0
Lafun	25	4.1	5.0	6.5	7.0	7.6	8.5	9.5
	32	4.0	4.6	6.1	6.3	6.5	7.4	8.5
Yam								
Instant pounded yam flour	25	4.8	5.8	6.2	7.6	8.6	8.9	12.5
	32	4.6	5.0	6.0	7.0	8.2	8.5	11.6
Elubo	25	4.5	5.2	6.5	8.5	9.0	9.5	11.1
	32	4.0	5.0	6.3	8.1	8.3	9.0	10.3

Values are expressed in percent on moisture free basis.

were very close for products with similar processing history (Mazza 1982). For relative humidity corresponding to 35% the equilibrium moisture content ranged from 4.5 to 7.5% at temperatures between 24–32 °C. Temperature and relative humidity affect equilibrium moisture values (Inglesias *et al.* 1986).

Sorption isotherm curves for gari and instant pounded yam flour which had similar processing conditions are shown in Fig. 1 and 2. The S shape of the curves are typical as for most starchy foods (Cripiste and Rotstein 1982).

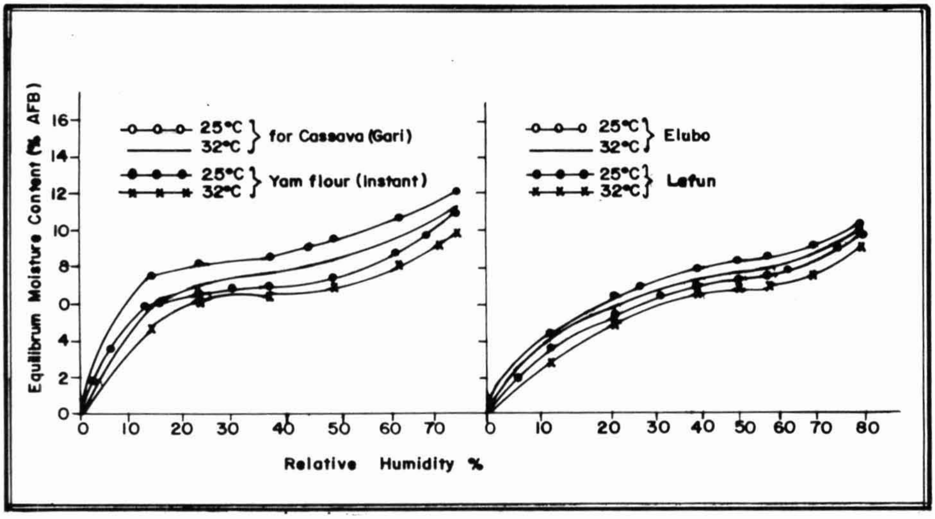

FIG. 1. MOISTURE SORPTION ISOTHERM FOR GARI AND INSTANT POUNDED YAM FLOUR

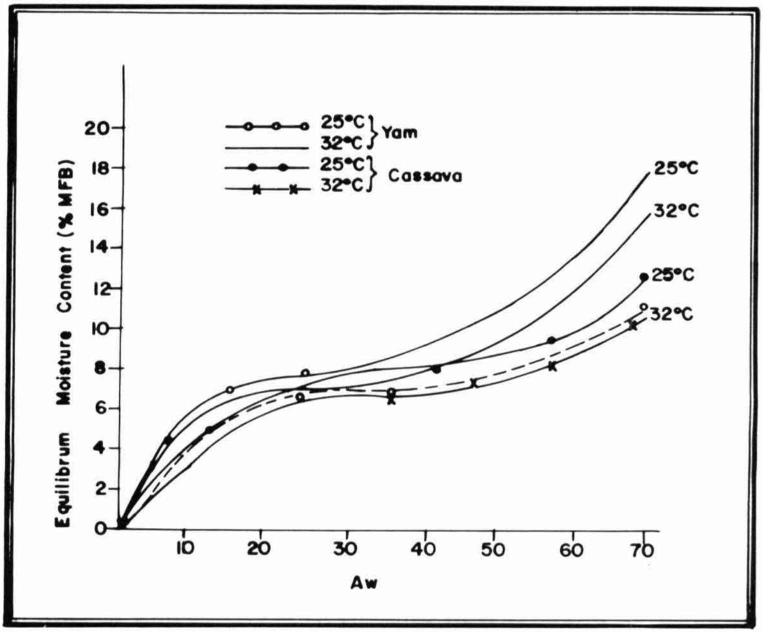

FIG. 2. MOISTURE SORPTION ISOTHERM FOR ELUBO (CASSAVA) LAFUN (YAM) PRODUCTS WERE NOT GELATINIZED

The optimum moisture content is calculated from the equilibrium moisture data by using the BET equation. The isotherm in the RH range of 5–35% was transformed to give a straight line BET plot. From the BET plot intercept I and slope Y were found and monolayer value b_1 (g H_2O/100 g dry material) was calculated from the following equation

$$b_1 = I/(I \times 100Y)$$

Many isotherm equations similar to the above are available in the literature, and these have been reviewed by Bruin *et al.* (1980). For gari and instant pounded yam flour the monolayer values were 4.0 to 6.5 g water/100 g solids at relative humidities below 40%. These values increased from 7.4 to 9.5 at 70%. In general the equilibrium moisture content decreased as the temperature increases.

The monolayer water content for starchy foods generally vary according to the composition and processing treatments. For potato products the calculated monolayer water content range from 5.1 to 5.8% (wet basis) for most dehydrated food products, Salwin (1963) showed that monolayer value in the range of 5.4–7.0% is suitable for storage stability. From this data, the calculated moisture value 4.0 to 9.5 were far lower in these products than the moisture levels of 13–15% recommended to assure stability of Nigerian foodstuffs

TABLE 2.
TASTE PANEL SCORES FOR THE STORED CASSAVA AND YAM PRODUCTS AT 32 °C[1]

Products	Storage time (months)	Freshly made products control (11-12% moisture)		Products as normally sold (11% moisture)		Products dried to within E.M.C. calculated (6.5-8.0%)	
Cassava		Dry	Reconstituted	Dry	Reconstituted	Dry	Reconstituted
Gari	1	8.2	7.2	7.3	6.1	8.3	7.3
	2	6.3	6.3	5.4	4.2	8.1	6.0
	3	4.1	6.3	2.5	3.3	6.0	5.8
Lafun	1	6.4	6.5	6.4	5.2	7.1	7.2
	2	5.3	5.3	5.5	4.4	6.3	6.5
	3	4.4	4.2	4.5	4.3	6.4	5.3
Yam							
Instant pounded yam flour	1	8.3	7.2	7.3	7.5	8.2	7.0
	2	7.2	6.1	6.5	6.3	8.1	7.0
	3	6.3	5.2	5.8	4.4	7.6	6.8
Elubo	1	6.1	6.3	6.3	5.8	7.6	7.3
	2	5.2	5.2	5.4	4.3	7.1	5.4
	3	5.3	4.3	4.3	4.2	4.8	5.0

[1] Scores represent the average of 9 panelists and are based on a 9 point hedonic scale where 1 = unacceptable with off-flavor, 5 = slight change, 9 = acceptable quality.

(Adesuyi 1973). These products as they are generally found under distribution conditions usually contain moisture levels between 9.5 to 12.5% which may account for their short-shelf-life and moldiness.

Data from the taste panel evaluation indicate that the calculated monolayer moisture levels to which the products were subsequently dried and stored made them to be acceptable for one month and off-flavor was noted at two months interval as marked by the low scores, and became unacceptable at 3 months. Similar changes in flavor quality of potato flakes and granules which had similar processing history as yam and cassava products have been reported (Stephenson 1958 and Sapers 1972).

Products dried to their monolayer moisture level had impaired quality attributes especially at high temperatures above 32 °C, (data not shown) compared with those dried to moisture levels slightly above the monolayer values. This observation might be attributed to the exposure of the products to oxidative changes especially at high temperature.

Gari, elubo, lafun and instant pounded yam flour dried and stored with moisture levels between 6.5 to 8.0% were acceptable in the dried form and upon reconstitution up to the end of the storage period in comparison with the controls. The color and flow properties of the products were not adversely affected at the end of the storage period.

The calculated monomolecular water layer and taste panel data confirm that the moisture levels at which yam and cassava products are generally manufactured are too high for their stability under current distribution practices. It is recommended that the products should be dried usually to a moisture level of 6.5 to 8.0% for good storage stability.

CONCLUSIONS

In summary, the moisture equilibria data indicated that for good storage stability, processed yam and cassava products should be dried to moisture levels in the range of 6.5–8.0%.

The taste panel data from the storage test confirm that off-flavor and other sensory attributes are not affected. Additionally, good packaging material which will prevent moisture absorption from the environment should be used in order to extend the shelf-life of these products.

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MODELLING DRY MATTER LOSSES FROM CARROTS DURING BLANCHING

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ABSTRACT

The mechanism of component losses from carrots during blanching was investigated by determination of reducing sugars, sucrose, total soluble solids and total solids in raw and variously blanched samples of Nantes carrots. The samples were 26 mm diameter, 26 or 60 mm long; blanching temperatures ranged 65–100°C and blanching times ranged 300–3600 s. Experiments were conducted using large amounts of well agitated water. Appropriate solutions of the unsteady state diffusion equation for finite cylinder geometry were used. The apparent diffusivities of each component were determined separately at different temperatures and resulting values correlated linearly or exponentially with temperature. The order-of-magnitudes of the apparent diffusivities were found to be 10^{-10}-10^{-11} m^2s^{-1} *and in good agreement with literature values.*

INTRODUCTION

The blanching operation, involved in almost all vegetable processing systems, results inevitably in losses of various solutes. Measurement of these losses and attempts to predict them have been the subject of various investigations (Holdsworth 1979; Lee 1958).

In addition to internal resistance to mass transfer, which can be expressed in terms of an apparent diffusivity, D_a (Stahl and Loncin 1979), resistance in the external liquid may also play a role if the medium is not sufficiently agitated. When the weight ratios of blanch water to vegetables are not large, the situation is further complicated by the variation of solute concentration in the blanch medium with time (Schwartzberg and Chao 1982).

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In any case, unidirectional unsteady state diffusion is given by (Spaninks 1979):

$$\frac{\partial C}{\partial r} = \frac{1}{r^{v-1}} \frac{\partial C}{\partial r} \left[r^{v-1} D_a \frac{\partial C}{\partial r} \right] \qquad (1)$$

where $v = 1$ for an infinite slab, 2 for an infinite cylinder and 3 for a sphere. The boundary conditions depend on whether the initial solute concentration is uniform, whether the external mass transfer is significant and whether concentration in the external medium remains constant throughout or changes with time.

Analytical solutions of (1) in terms of dimensionless variables for concentration, $Y = (C\text{-}C_s)/(C_o\text{-}C_s)$, time, $\tau = D_a.t/r_o^2$, position, $x = r/r_o$ and so on for various geometries are given in Crank (1975) in series forms. In some cases, more than one series solutions are given for the same set of conditions, each converging rapidly for different numerical values of variables. In most cases, the solutions are also transformed into an expression for average solute concentration, $\overline{Y}$, obtained by integrating the concentration over the entire volume. For finite geometries, Chorny and Krasuk (1966), Bressen *et al.* (1981a) and Giannakopoulos and Guilbert (1986) have applied Newman's rule (Treybal 1968), obtaining the finite body as the intersection of infinite geometries by multiplying the corresponding solutions.

Solution types appropriate for leaching operations carried out under various conditions, along with the limitations of their applicability are given in Schwartzberg and Chao (1982); in which an extensive list of apparent diffusivity values in foods is also reported, including those for soluble solids and sucrose in sugar beets and apple slices. Califano and Calvelo (1983) determined the apparent diffusivity of reducing sugars in potato. Selman and Rolfe (1979) investigated solute losses from peas and carrots and found that contraction of tissues upon loss of cell turgor was an important factor. Bressan *et al.* (1981b) correlated the effective diffusion coefficient for total solids during the washing of cheese curd linearly with temperature. Selman *et al.* (1983) measured losses of soluble solids on 5–7 mm diameter, 60 mm long cylinders cut from cores or cortexes of Chantenay carrots and of an unidentified cultivar and correlated the apparent diffusivities, which were similar in samples from cores or cortexes, exponentially with temperature.

MATERIALS AND METHODS

Materials

Nantes carrots, grown in Beypazari, Ankara were used in this study. Carrots with uniform diameters and lengths were stored for 1–2 months at 0–4 °C at 80–90% relative humidity before the experiments. The outermost layers were removed and the carrots were cut to produce 26 mm diameter cylinders, 26 or 60 mm long. In order not to compound diffusion phenomenon with temperature gradients, samples were wrapped in aluminum foil and exposed to steam until the temperature at their thermal centers reached the desired temperature of the blanching experiment. Preliminary experiments showed that dry matter losses during such preheat treatments were below 0.1%.

Blanching

Blanching experiments were conducted using 4–12 carrot samples (120–135 g) placed in stainless steel baskets and lowered into 11 kg water in a thermostat bath at temperatures between 65–100 °C, controlled to within ±0.5 °C. Treatment durations ranged 300–3600 s, the blanching medium being well agitated via two propellers at 2200 rpm, facilitating negligible external resistance to mass transfer. Samples were placed into sealed containers upon completion of blanching and immediately cooled in ice to 20 °C in order to minimize evaporation losses.

Analytical Methods

The raw and blanched carrot samples were homogenized in a Waring blendor and analyzed for total solids and soluble solids according to procedures given by the Association of Official Analytical Chemists (AOAC, 1975). The mono- and di-saccharides in carrots are reported to be glucose, fructose and sucrose (Southgate 1976). The Lane-Eynon method for determination of reducing sugars and total sugars, as given by AOAC (1975), was used for the determination of reducing sugars and sucrose. All analytical determinations were carried out in duplicate.

Mathematical Solution

Under the blanching conditions described above, boundary conditions for initially uniform solute concentration, negligible external resistance and negligible solute concentration in the blanching medium are valid. Literature values and the preliminary evaluation of the experimental results for the order-of magnitude of the apparent diffusivities revealed that the series solution given in Crank (1975) and also suggested by Schwartzberg and Chao (1982) converging rapidly for short times are the most appropriate for this case. The numerically significant terms of these solutions for the average concentration for the infinite geometries are given below:

Infinite slab:

$$\bar{Y}_1 = 1 - 2\sqrt{\frac{\tau_1}{\pi}} \tag{2}$$

Infinite cylinder:

$$Y_c = 1 - \frac{4}{\sqrt{\pi}} \sqrt{\tau_c} - \tau_c - \frac{1}{\sqrt[3]{\pi}} \tau_c^{1.5} \tag{3}$$

The solution for the finite cylinder is obtained as:

$$\bar{Y}_{c1} = \bar{Y}_1 . \bar{Y}_c \tag{4}$$

For different values of the term $D_a.t$, and values of c and 1, τ_c and τ_1 values and the corresponding $\bar{Y}_{c1}$ values were determined and stored in tabular form. For each experimental $\bar{Y}_{c1}$, the corresponding $D_a.t$ was estimated by interpolation from these values. Hence, an array of $D_a.t$ values versus experimental t values were obtained for blanching of different size carrot samples for different lengths of time at various constant temperatures. The corresponding apparent diffusivity was obtained as the slope by linear regression of values $D_a.t$ to t.

Statistical Evaluation

The series of blanching experiments at one of the temperatures was replicated in order to facilitate analysis of variance comparing lack of fit and pure error (Draper and Smith 1966).

RESULTS AND DISCUSSION

The concentration of various components in raw carrots are given in Table 1, and the results of blanching experiments are summarized in Table 2.

The applicability of the procedure used for determination of apparent diffusivity is illustrated in Fig. 1 and 2, which are plots of $D_a.t$ vs t values obtained from experimental data.

TABLE 1.
COMPOSITION OF RAW CARROTS

		Concentration, % Wet Basis	
Component	Range	Mean	Coeff. of Var.
Total solids	9.7 - 12.5	11.9	0.10
Soluble solids	7.0 - 9.4	8.9	0.12
Sucrose	1.9 - 2.8	2.4	0.22
Reducing sugars	2.7 - 3.6	3.2	0.16

TABLE 2.
RANGES OF COMPONENT LOSSES DURING BLANCHING

	Percentage Losses at		
Component	65 °C (600–3600s)	80 °C (300–1800s)	100 °C (300–1800s)
Total solids	1.6 - 19.2	1.6 - 25.8	4.0 - 29.6
Soluble solids	2.1 - 23.4	1.1 - 30.0	4.3 - 29.6
Sucrose	5.2 - 26.3	7.1 - 28.5	28.6 - 46.4
Reducing sugars	5.6 - 33.3	3.7 - 29.6	3.7 - 40.7

The analysis of variance, made on the replicated experiments at 65 °C resulted in ratios of lack of fit sum of squares to pure error sum of squares of 0.21–5.99 compared to the F value of 6.94 at a probability level of 5%, indicating the model to be adequate. The randomness of deviations from linearity and closeness of points for different length samples are also in support of the adequacy of the suggested model of constant diffusivity. The positive value of the time intercept is probably due to the changing permeability of the cell walls during the first few minutes as suggested by the work of Selman and Rolfe (1979).

The dependence of apparent diffusivity on temperature can be seen in Fig. 3, along with apparent diffusivity values of different components for similar material reported in the literature.

Comparison of results from the present study with those reported in the literature show surprisingly similar values of diffusivities of reducing sugars, sucrose and total soluble solids in carrots with those in apple slices, potato and sugar beet. The value reported for an unidentified carrot cultivar by Selman *et al.* (1983) correlates well with the values obtained in this study. The values reported for Chantenay carrots by the same authors are somewhat lower for temperatures greater than 70 °C.

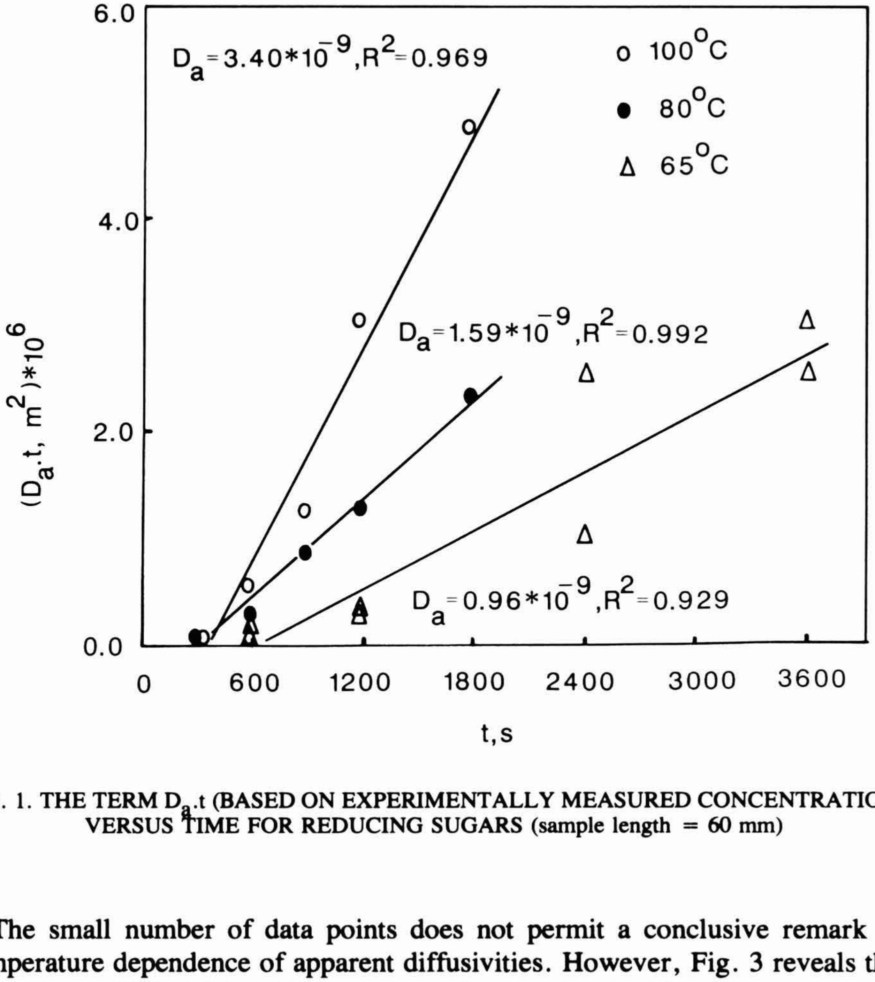

FIG. 1. THE TERM D_a.t (BASED ON EXPERIMENTALLY MEASURED CONCENTRATION) VERSUS TIME FOR REDUCING SUGARS (sample length = 60 mm)

The small number of data points does not permit a conclusive remark on temperature dependence of apparent diffusivities. However, Fig. 3 reveals that the apparent diffusivities of the sugars can be correlated with temperature according to an Arrhenius type of expression.

The parameter values obtained by least square fits to the experimental points are given below:

Reducing sugars $D_a = 0.63*10^{-3}\exp(-4.54*10^3/T(K))$ (5)
Correlation coefficient = 0.997

Sucrose $D_a = 11.2*10^{-3}\exp(-5.64*10^3/T(K))$ (6)
Correlation coefficient = 0.997

The activation energies of 37.6 and 46.8 kJ/mol for the reducing sugars and sucrose, respectively, indicate somewhat stronger temperature dependence in

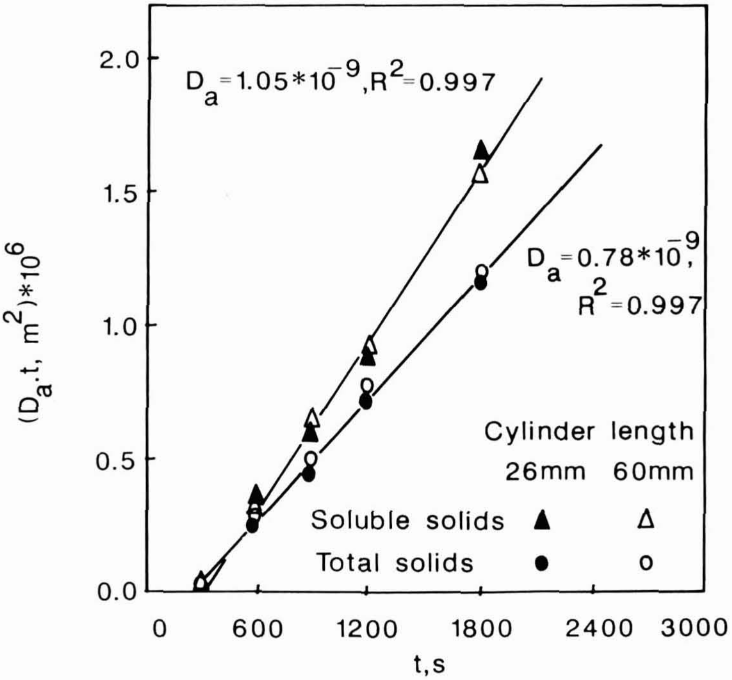

FIG. 2. THE TERM D_a.t (BASED ON EXPERIMENTALLY MEASURED CONCENTRATION) VERSUS TIME AT 80 °C FOR DIFFERENT LENGTH SAMPLES

the case of sucrose. Diffusion of sugars in a liquid phase is not normally expected to be an activated process. The pronounced effect of temperature is more likely to be due to temperature effects on the permeability of the carrot matrix.

Experimental results on apparent diffusivities of soluble solids and total solids indicate significant curvature on the Arrhenius plot, falling on straight lines when plotted linearly against temperature. The limited number of data points may contribute to this observation. The equations for these lines, obtained also by least squares fits are given below:

Soluble solids
$$D_a = 3.48*10^{-11}\ T(K) - 1.13*10^{-8} \tag{7}$$
Correlation coefficient = 0.994

Total solids
$$D_a = 3.67*10^{-11}\ T(K) - 1.21*10^{-8} \tag{8}$$
Correlation coefficient = 0.999

Materials defined as soluble solids or total solids are made up of components such as sugars, mineral salts, vitamins, pectic and cellulosic substances, and the

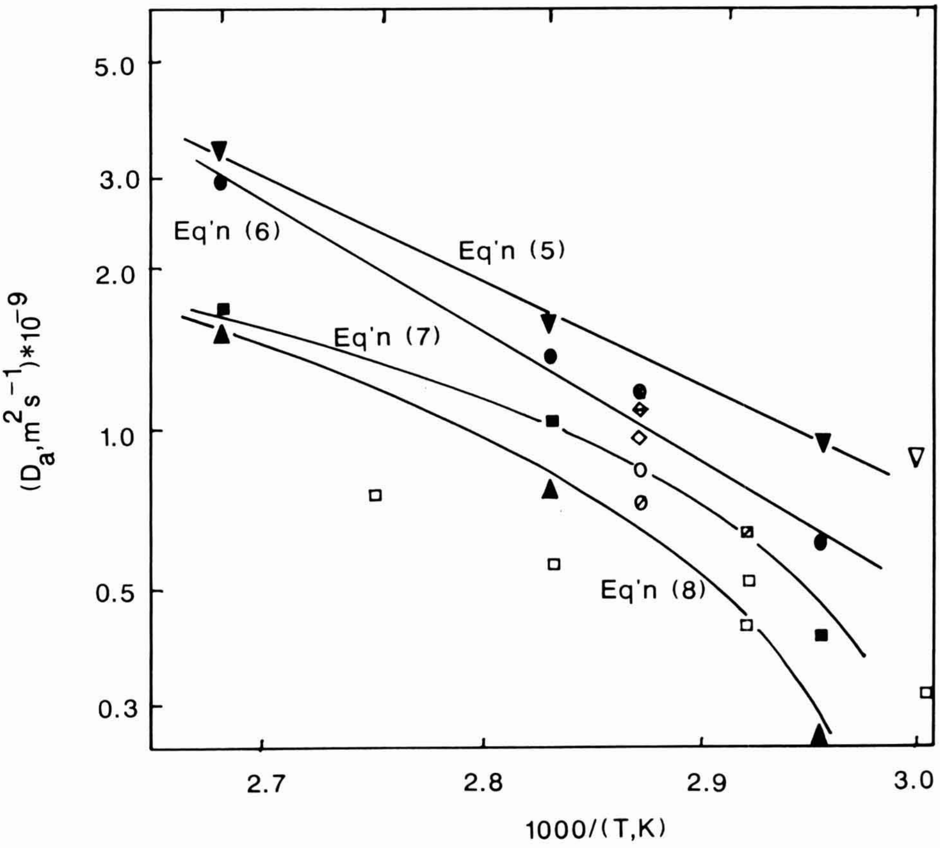

FIG. 3. ARRHENIUS PLOT OF APPARENT DIFFUSIVITIES

▼	Reducing sugars	Nantes carrots	Present study
●	Sucrose	Nantes carrots	Present study
■	Soluble solids	Nantes carrots	Present study
▲	Total solids	Nantes carrots	Present study
□	Soluble solids	Chantenay carrots	Selman *et al.* (1983)
⧄	Soluble solids	unidentified carrots	Selman *et al.* (1983)
⊖	Soluble solids	apple slices	Vukov and Monszpartsenyi (1977)
◇	Soluble solids	sugar beets	Bruniche-Olsen (1962)
⊗	Sugars	apple slices	Vukov and Monszpartsenyi (1977)
⊘	Sucrose	sugar beets	Bruniche-Olsen (1962)
○	Sucrose	sugar beets	Vukov and Monszpartsenyi (1977)
∇	Reducing sugars	potatoes	Califano and Calvelo (1983)

form of overall temperature dependence can hardly be attached to physical significance. The apparent diffusivity of nitrate in carrots, for example, is reported to be four times as much as the value for total solids under similar conditions (Varoquoux *et al.* 1986). The behavior of components so different from one another would probably be affected by temperature in different different ways; and hence, when lumped into a single, 'pseudo' constant D_a along with temperature effects on the matrix structure, the overall result may be a linear variation with temperature. It is reported by Griswold (1962) and Anderson and Clydesdale (1980) that some of the insoluble components may also convert into soluble ones during wet heat processing, changing the amount of total extractable substances. Correlations obtained in this study are considered to be empirical relations enabling the estimation of losses of variously defined components during blanching of carrots.

CONCLUSIONS

(1) Losses of reducing sugars, sucrose, soluble solids and total solids during water blanching of carrots can be characterized with an average, or 'pseudo' diffusion coefficient whose temperature dependence is Arrhenius type of linear.

(2) The processing losses in commerical blanching operations can be predicted using the correlations presented here for the apparent diffusivities along with the form of mathematical solution appropriate for that particular case. Losses from slices or cubes into large amounts of blanching water can readily be estimated. In the case of limited amount of blanching water, information on external mass transfer coefficient would also be required.

(3) The information on apparent diffusivity would also aid in optimizing processes and equipment design.

NOMENCLATURE

c = Cylinder radius, m
C = Solute concentration in the solid, %; C_o, the original; C_s, at the surface; $\overline{C}$, the average
D_a = Apparenent diffusivity, m^2s^{-1}
l = Slab half thickness or cylinder half length, m
r = Distance from the center of object, m; r_o, at the surface
Y = Solute concentration ratio, $(C - C_s)/(C_o - C_s)$; $\overline{Y}$, based on $\overline{C}$ instead of C
τ = Dimensionless variable for time (mass Fourier number), $D_a.t/r_o^2$

Subscripts

c = For infinite cylinder
cl = For finite cylinder
l = For infinite slab

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MODELLING OF TEMPERATURE HISTORIES DURING VENTING OF STILL RETORTS

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ABSTRACT

Experimental tests were carried on a pilot retort to gather information on the temperature evolution inside batch retorts during the venting stage. To fit the coming-up curves the equation for the response of an over-damped second-order system to a step input was proposed. The parameters that characterize this equation were related to steam flow, initial temperature and retort load. Results allow the prediction of coming-up curves for different operating conditions.

INTRODUCTION

The purposes of this study were to find an adequate method to predict the temperature evolution inside retorts during venting and to establish the way in which temperature evolution during venting is affected by changes in the operating conditions.

Steam batch retorts are still widely used due to the low initial cost (Manfre 1969) and to the flexibility of processing different products in different cans.

Information about the way the venting is affected by changes in the operating conditions is scarse. Bhownik and Hayakawa (1983) observed that the amount of steam used during the come-up time was moderately higher with a lower initial food temperature at the same retort temperature.

Felmingham and Leigh (1966) presented venting curves for different venting procedures and different retorts.

To estimate food temperature for a come-up heating process changes in heating medium temperature during venting should be known. Most formulas applicable to the estimation of thermal processes were obtained assuming simplified relationships between surface temperature and processing time

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(Hayakawa and Ball 1971). Merson *et al.* (1978) recommended that research be undertaken to verify the method, first introduced by Ball (1923), of considering 42% of the coming-up time to be lethal. To estimate food temperatures by a computational procedure Hayakawa (1971) approximated the time variable ambient temperate with a combination of step changes. Hayakawa and Ball (1971) used a linear and a quadratic approximation of the come-up curves to derive expressions for estimating sterilizing values during a come-up period. Uno and Hayakawa (1980) used an exponential formula to represent venting curves.

In this work we propose a model to predict the temperature evolution during venting based on a physical interpretation of the system and present an expression to evaluate the effect of steam flow and initial temperature on the venting curves. We also show the influence of changes in the retort load.

MATERIALS AND METHODS

The retort used in the tests is depicted in Fig. 1. The horizontal cylindrical retort was geometrically similar to industrial equipments. The length was 1.12 m, the inside diameter was 0.35 m and the volume of the empty retort was approximately 0.09 m^3. A steam spreader (internal diameter = 0.019m) ran along the bottom of the retort and was connected to the external steam pipe at the mid-point in the bottom of the retort. Two rows of 28 holes (diameter = 0.0026m) each were arranged in the top 90° of the spreader. The venting line (internal diameter = 0.025 m) was connected at the mid-point on the top of the retort. Condensate was removed through a pipe (internal diameter = 0.013 m) connected to the bottom of the retort. There was a 0.008 m bleeding cock at each end of the retort.

The cans were chosen to keep approximately the geometrical scale factor existing between the experimental and industrial retorts. The aluminum cans (diameter = 0.00385 m,.height = 0.0135 m) were filled with minced fish (α = 0.074 ± 5.9% cm^2/min). A total of 1700 cans were jumble packed in two crates made of wire mesh on an iron structure.

A mercury in glass thermometer with protecting well was placed in a chamber connected to the retort by a 0.019 m diameter opening. This chamber was fitted with a 0.008 m bleeding cock. Cooper-constantan thermocouples and an Ellab Z4FD recorder (Ellab Instruments, Copenhagen) were used to record temperature at different locations in the retort.

Condensate was collected in a graduated container. The steam header (diameter = 0.025 m) was fitted with a filter, a condensate trap and a self-regulating valve that kept the supply pressure at 392 kPa gauge. An orifice meter (β = 0.6) was installed on the supply line. The flange taps were connected through a manifold to the branches of a mercury inclined manometer. The orifice meter and the manometer were especially calibrated for the tests.

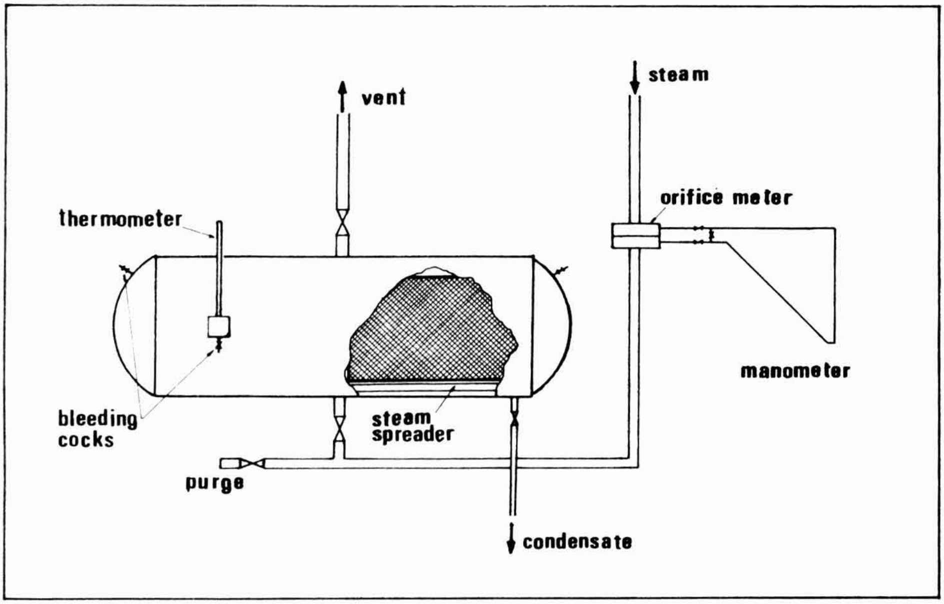

FIG. 1. SCHEMATIC VIEW OF THE EXPERIMENTAL RETORT

Before each experiment the supply line was purged to eliminate all condensate. To start venting the purging valve was closed and the ball valve on the retort inlet line was opened simultaneously. The vent valve, the bleeding cocks, and the drain were kept completely open during the tests. The amount of condensate and the readings of the mercury in glass thermometer were recorded every 10 to 15 s. Venting was continued until all thermocouples readings reached 100 °C.

Experiments were performed with different steam supplies, different initial temperatures and different retort loads. The equation for the response of an overdamped second-order system to step inputs was fitted to the curves of temperature evolution. For this purpose the slope-intercept method described by Douglas (1972) was used.

RESULTS AND DISCUSSION

Temperature evolution in various locations of the retort were monitored during venting. Temperature rises among the cans were highly dependent on the location. Points located just over the steam spreader, i.e. at the bottom of the crates, reached 100 °C almost instantaneously. On the other hand the slowest heating point was found to be among the cans near the center of the retort.

O'Connor (1976) and Lopez (1975) recommend that a mercury thermometer must be used to determine the retort temperature. However, the temperature rise in the thermometer chamber was particularly slow in our experiments. Also the dynamics of the thermometer itself made the readings to lag the actual temperature in the chamber. In our tests the thermometer readings had never reached 80 °C by the time all thermocouple readings had reached 100 °C. Therefore we decided not to use thermometer readings to characterize the venting stage. Instead we used the temperature indicated by the thermocouple in the void space above the crates to characterize the venting. This location is easy to reach and results are more reproducible because they are not affected by the position of cans that may affect the other thermocouple readings. The temperature rise in this location was intermediate between the fastest and slowest venting curves and it was similar to the temperature rise in the center of the can load (see Fig. 2).

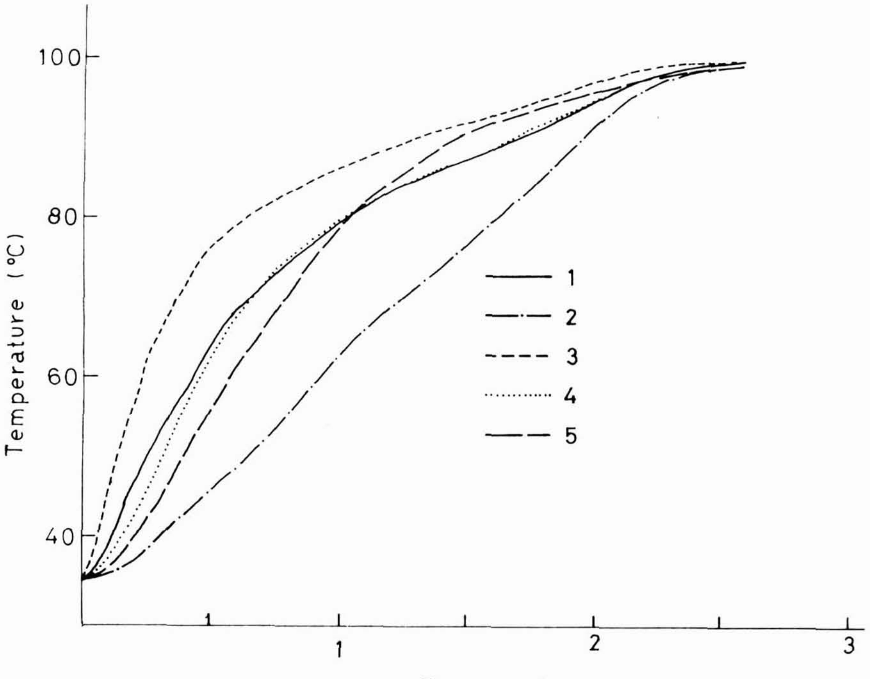

FIG. 2. THERMAL HISTORIES DURING VENTING AT: (1) void space over the load; (2) mid-level of loaded crate near center of retort (slowest heating area); (3) mid-level of loaded crate near end of retort and (4) center of crate; (5) second order fit to curve 1. (T_1 = 0.56 min, T_2 = 0.29 min)

The formula proposed by Uno and Hayakawa (1980) to fit coming-up curves was tried on our data. Although it could be used to represent accurately the later half of the coming-up curve we could not achieve a good fit over the whole curve, which is needed to define temperature gradients within the food container. On the other hand it represents an empirical approach that requires the original coming-up curve and therefore can not be used to make predictions when the operating conditions are changed.

Condensate collected at the beginning of the venting stage correspond to most of the steam introduced in the retort. Therefore most of the steam must overcome the resistence represented by the cold cans before it participates actively in the air removal. Physically, this implies that the retort behaves like two interacting subsystems; the can load and the void space from which air must be removed. A feature of the response of systems higher than first order to step inputs is a zero initial slope. All the venting curves in our experiments presented a zero initial slope. This feature is also commonly found in coming-up curves reported in the literature (Thijssen and Kochen 1980; Hickman and Robinson 1973). The response of a series of two first order systems (or an overdamped second-order system) to a step input is (Harriot 1974).

$$\phi_t = 1 + \frac{1}{T_1 - T_2}(T_2 e^{-t/T_2} - T_1 e^{-t/T_1}) \tag{1}$$

Where T_1 and T_2 are the time constants and ϕ is the fractional response of the system.

In our case

$$\phi_t = (\theta_t - \theta_i)/(100 - \theta_i)$$

with θ_t temperature and θ_i initial temperature.

There are several methods to estimate T_1 and T_2. We chose the slope-intercept method because it takes under consideration all the experimental data (Douglas 1973).

Equation (1) is also represented in Fig. 2 for the corresponding experimental curve.

Different steam flow rates may be desired to produce changes in venting curves to optimize product quality, or minimize temperature gradients in the retort and steam consumption. We tested steam flows in the range of 0.45 to 2.28 kg/min.

Can temperature at the start of the process depends on several factors, such as the filling method or the time elapsed from cooking or blanching to sterilization. Therefore we carried out tests varying the initial temperature in the range from 17 to 62.5 °C.

At the end of a working day it is usual to sterilize with the retort not fully loaded. To investigate the effect of partial loads on venting curves we performed tests with 4/5, 3/5 and 2/5 of a full load.

To determine reproducibility of results, tests were performed for the same load, initial temperature and steam flow. In these experiments the greatest temperature difference for any of the monitored locations in the retort, at any given time, never exceeded 5 °C.

In all tests the temperature evolution in the void space above the crates was adjusted to equation (1) by means of the slope intercept method. The T_1 versus T_2 values were fitted to a straight line by statistical regression analysis.

$$T_2 = 0.033 + 0.502\ T_1 \qquad (2)$$

$$r = 0.973 \qquad (n=20)$$

Therefore to predict the temperature evolution from Eq. (1) the value of only one time constant would be required.

The largest time constant was related to steam flow and initial temperature. From statistical regression analysis the following expression resulted.

$$T_1 = 18.11 \times W^{-0.805} \times \theta_i^{-0.726} \qquad (3)$$

$$r = 0.931 \qquad (n = 20)$$

Where W is the mass steam flow in kg/min and θ_i the initial temperature in °C.

The two subsystems are interacting, that is the thermal history within the load is not independent of changes ocurring in the void space around the cans. Therefore the time constants can not be assigned to each subsystem independently and should be considered as effective time constants as a result of the interaction. The effect of partial load on the ratio of both time constants and on the largest time constant (as a fraction of the largest time constant for full load) is shown in Fig. (3). The fact that the thermal capacity of the system and the resistance to the steam flow decrease as the retort load is reduced could explain these results. When the empty retort was vented, that is when one of the subsystems had been removed, the system behaved like a first order system with a nonzero intial slope.

In conclusion, the response of an over-damped second-order system to a step input is proposed to fit venting curves. The time constants that characterize this response have been related to steam flow, initial temperature and retort load.

The scaling-up of these results should only be possible to geometrically similar retorts. Nevertheless the proposed method may be used to characterize the behavior of other retorts with different constructive details.

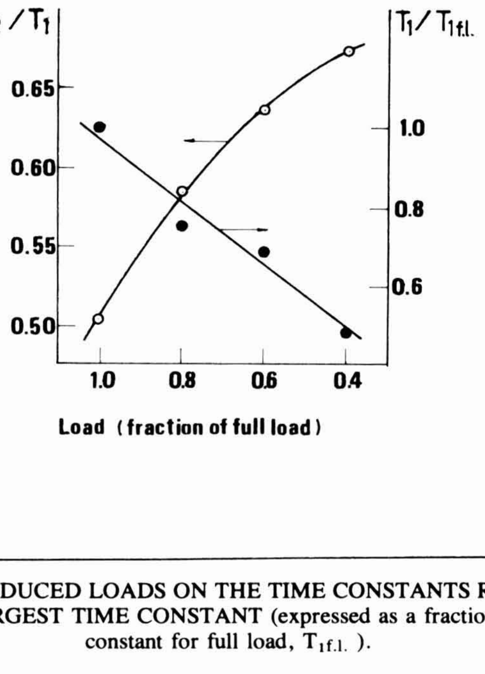

FIG. 3. EFFECT OF REDUCED LOADS ON THE TIME CONSTANTS RATIO AND ON THE VALUE OF THE LARGEST TIME CONSTANT (expressed as a fraction of the largest time constant for full load, $T_{1f.l.}$).

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CRYOGENIC SEPARATION OF CITRUS FRUIT INTO INDIVIDUAL JUICE SACS

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ABSTRACT

Citrus fruits were crushed by a falling ball type impact crusher at low temperature and their juice sacs were separated into individual sacs. The effect of freezing temperature on the degree of separation was examined, using four kinds of citrus fruits, Unshu orange, sweet orange, grapefruit, and lemon. The results indicated that the degree of separation depended solely on temperature regardless of sample size, applied force, and fruit kind. No shattering occurred above −30°C. The degree of separation increased until below −120°C, there was little further separation. The cause of no shattering at or above −30°C was attributable to the mechanical property of juice.

INTRODUCTION

There has been an increasing interest in cryogenic method using liquid nitrogen for size reduction of foodstuffs. This is mainly because the amount of available liquid nitrogen is getting greater with increasing consumption of LNG (liquified natural gas), particularly in Japan (Takashima 1982). When fuel gas is produced from LNG, its heat of evaporation is used as the low temperature heat sink in liquifying nitrogen. Most of applications of cryogenic size reduction is the grinding of foodstuffs into their fine powders with high quality. Its advantages over the conventional methods are: fatty and moist materials can be easily ground, liquid nitrogen removes the evolved heat, and nitrogen makes an inert atmosphere (Wistreish 1962; Andres 1976; Yamaguchi 1979; Hagihara 1982; K.H.H. Shemsanga 1985).

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Another application of cryogenic size reduction is the separation of agglomerated granules, such as juice sacs in a citrus fruit and eggs in a roe, into individual granules. In some factories, individual juice sacs are manufactured by a cryogenic crushing method. To Japanese consumers, separate juice sacs in a citrus fruit beverage contribute to visual appeal, mouth feel and body and the connotation of 'fresh-squeezed' juice. However, there have been published few reports on the application of cryogenic crushing to separation of agglomerated foodstuffs into individual granules.

In cryogenic processes, the product cost is governed by operating temperature (Kobayashi 1979). The present paper, which deals with the effect of temperature on separation of citrus juice sacs, shows that the separation occurs only at or below −40 °C and the freezing at −120 °C sufficiently works.

MATERIALS AND METHODS

Citrus Fruits

Unshu orange (*Citrus Unshu*), sweet orange (*C.sinensis*), grapefruit (*C. paradisi*), and lemon (*C. Lemon*) were used. Either a whole of a section (loculus) or a central part (20 mm in length) remaining after cutting off the both ends of a section (Fig. 1) was used. The former is called a whole sample and the latter a cut sample in this paper. These samples wrapped in polyethylene films were frozen at various temperatures from −20 °C to −196 °C. An air blast freezer was used for freezing at −20 °C to −40 °C and at −100 °C, acetone-solid carbon dioxide cooling mixture at −88 °C, and liquid nitrogen at −196 °C. The temperatures of samples were monitored in progress of freezing using a thermocouple inserted at the center of a dummy sample. The periods of time required to cool the samples to the predetermined temperatures were measured. After the frozen sample was held at each preset temperature for a period which is three times longer than the period required to bring it to the temperature, polyethylene film was removed. Immediately after it, the sample was subjected to the experiment.

Ice Cubes

Ice cubes of size of 20 × 20 × 20 mm were prepared from degassed pure water (Japanese pharmacopoeia) and from sweet orange juice in an air blast freezer at −15 °C to −100 °C.

Apparatus

A falling ball type impact crusher depicted in Fig. 2 was used. A sample cooled at a predetermined temperature was struck by a ball dropped through a vertical tube. Fragments produced were gathered in a collecting box. A stopper plate prevented successive blows which damaged the separated juice sacs. The weight and diameter of the ball made of stainless steel were 68.1 g and 2.54 cm, respectively.

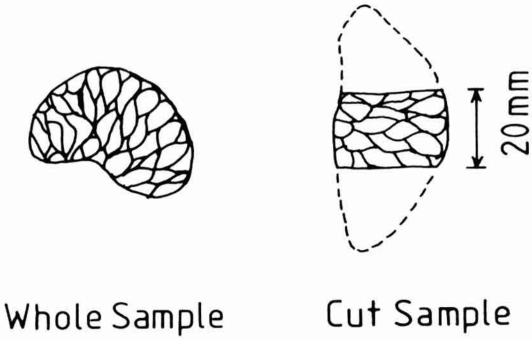

FIG. 1. SHAPE AND SIZE OF SAMPLE

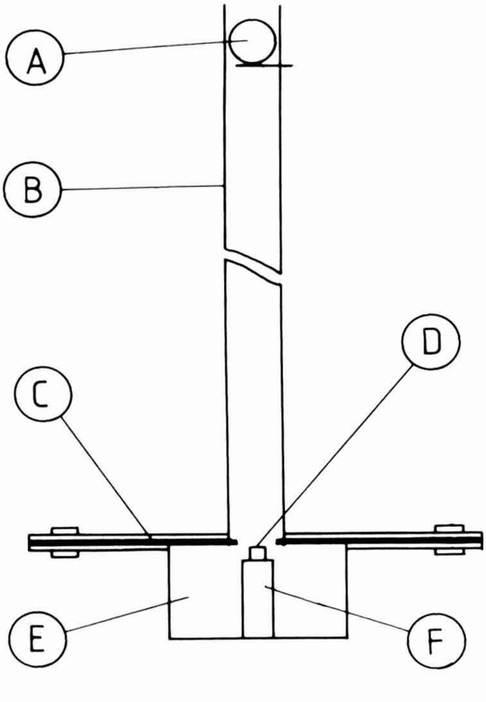

FIG. 2. A SCHEMATIC DIAGRAM OF THE FALLING BALL TYPE IMPACT CRUSHER

A: Falling ball
B: Guide tube
C: Stopper plate
D: Test piece
E: Fragment receiver
F: Test piece table

Procedure

A frozen citrus fruit sample set on the test piece table was struck by the ball fallen from the height of either 0.5 m or 1.0 m in a room maintained at a temperature below 7 °C. The fragments produced by the impact was collected and their number was counted.

Ice cube samples of pure water and citrus juice were struck in the same manner as fruit samples at a room temperature lower than −15 °C. The fragments were counted after removing fine powders through a sieve with a 2 mm opening. Although the thawing of fruit fragments did not hinder the counting, that of ice cubes did by a great deal. Therefore, the ice cube samples were struck at a temperature low enough to prevent thawing.

RESULTS AND DISCUSSION

In order to describe the effect of impact, the degree of separation, ξ, was defined as

$$\xi = (N - 1) / M$$

where M is the total number of juice sacs in the sample, N is the number of the fragments produced by the impact of the ball on the sample. The degree of separation ranges from 0 to 1.

Cut samples of Unshu orange cooled to various temperatures were struck by the ball dropped from a height of 1.0 m. The result shown in Fig. 3 indicates that no separation took place at or above −30 °C. On the other hand, at or below −40 °C, as the temperature decreased there was an increase in degree of separation.

The results of shattering other samples showed similar dependence on temperature, although the degree of separation was different with different kinds of fruit and with experimental conditions. When the ratio of the degree of separation at a temperature, ξ, to the degree at −196 °C, ξ_{-196}, is plotted against temperature (Fig. 4), the figure shows that the ratio solely depended on temperature regardless of the size of the samples, applied force to the samples, and the kind of fruit. Figure 4 shows no shattering appeared when temperature is at or above −30 °C, the ratio, ξ / ξ_{-196}, increased with decreasing temperature between −30 °C and −120 °C, and the ratio was nearly unit at temperature below −120 °C.

After the sample frozen at or below −40 °C was struck, it was visually observed that the sample was crushed into a number of juice sacs which were separated from one another and kept the original spindle-like shape for all their parts. The number of juice sacs which were in bits was counted and shown in a frequency

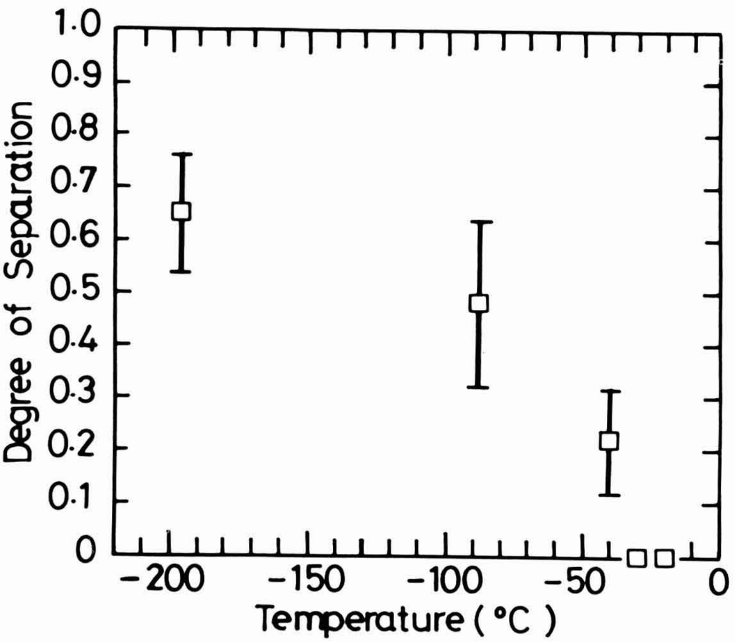

FIG. 3. THE DEPENDENCE OF TEMPERATURE ON THE DEGREE OF SEPARATION FOR CUT SAMPLES OF UNSHU ORANGE The height of ball drop is 1.0 m. Arithmetic mean and standard deviation are plotted. Standard deviations at −20 °C and −30 °C are nearly zero.

distribution chart (Fig. 5). On the contrary, as for the sample frozen at or above −30 °C, the separation into individual sacs did not take place and the sample only got a local damage at the vicinity of the hit point. It is interesting to examine the difference in pattern of shattering between the two freezing temperature ranges at or below −40 °C and at or above −30 °C. The possible causes that bring the difference are: (1) the property of juice, (2) the property of something which fills between the juice sacs, and (3) the property of the membrane of juice sacs.

To examine the case (1) a comparison was made, using ice cubes samples, between pure water ice and sweet orange juice with regard to their reaction to impact. The juice ice did not shatter if the temperature did not fall to −35 °C although the pure water ice did at temperatures slightly lower than 0 °C (Fig. 6). Since citrus fruit and its juice ice agreed with each other in their threshold temperatures above which no shattering was observed, no shattering of citrus fruit above the threshold temperature will be attributable to the mechanical property of its juice.

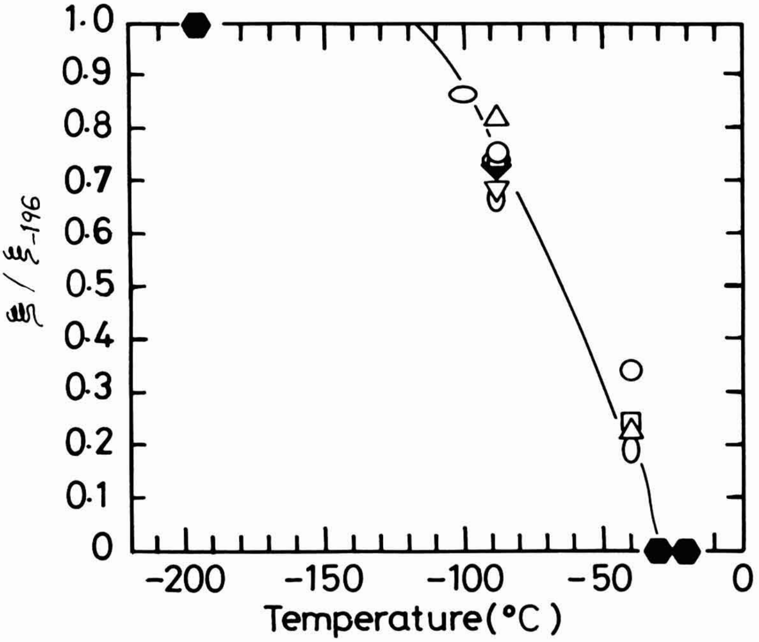

FIG. 4. THE RELATIONSHIP BETWEEN TEMPERATURE AND THE RATIO OF THE DEGREE OF SEPARATION AT A TEMPERATURE, ξ, TO THE DEGREE AT −196 °C, ξ_{-196}
Height of ball drop 1.0 m: whole sample of Unshu orange (△), cut sample of Unshu orange (○), cut sample of grapefruit (▽), cut sample of sweet orange (⬭), cut sample of lemon (▼). Height of ball drop 0.5 m: whole sample of Unshu orange (0), cut sample of Unshu orange (□). All data are overlapped at −20 °C, −30 °C, and −196 °C (⬢).

The freezing of citrus juice is considered to give a microscale mixture of pure water ice crystals and concentrated amorphous solution (CAS)(Bellows and King 1972). Since the pure water ice crystals were shown to be shattered above −35 °C, the cause of no shattering of juice ice should be in the mechanical property of CAS. Bellows and King (1972) studied the viscosity of CAS concerning collapse phenomena. They indicated that below the collapse temperatures CAS was highly viscous and acted as a structurally rigid solid. But CAS became more fluid above the collapse temperature. The collapse temperature of orange juice (−24 °C), grapefruit juice (−30.5 °C) and lemon juice (−36.5 °C)(Bellows and King 1972) nearly coincide with the threshold temperature (−30 °C ~ −40 °C) presented in the present work. This fact may allow the following speculation. Above the threshold temperature, a stress given on the surface of the juice ice by a blow is absorbed by mobile CAS and the propagation of the stress is prevented.

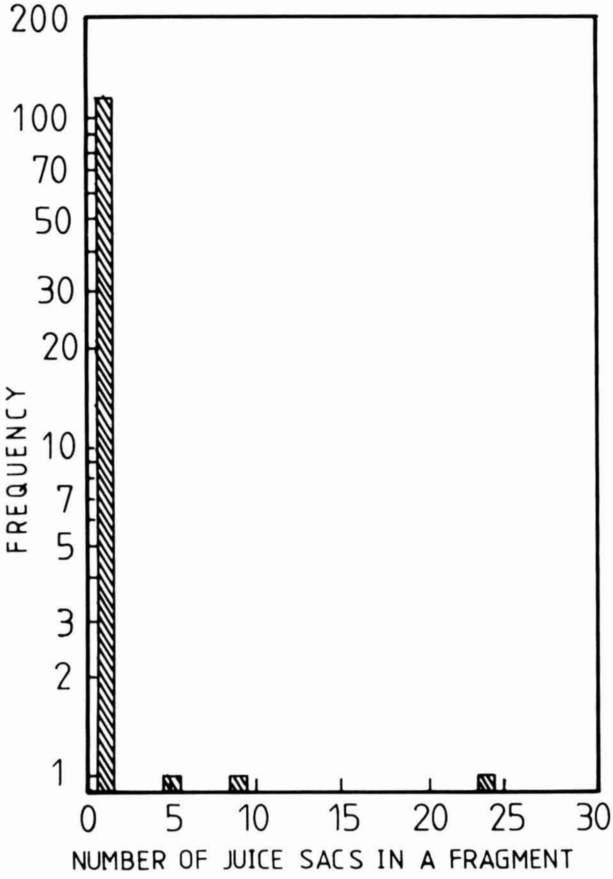

FIG. 5. A FREQUENCY DISTRIBUTION CHART OF THE NUMBER OF JUICE SACS IN A FRAGMENT PRODUCED BY THE IMPACT OF THE BALL
A cut sample of sweet orange frozen at −196 °C. Height of ball drop: 1 m.

Then the separation does not take place. On the contrary, when citrus fruit is frozen below −40 °C, CAS acts as rigid solid and allows the propagation of the stress which separates the juice sacs.

The conclusion to be drawn from the present results is as follows. For separation of citrus fruit into individual juice sacs, the material has to be frozen below the threshold temperature, −35 °C, and the freezing at the level off temperature, −120 °C, is good enough for maximum separation.

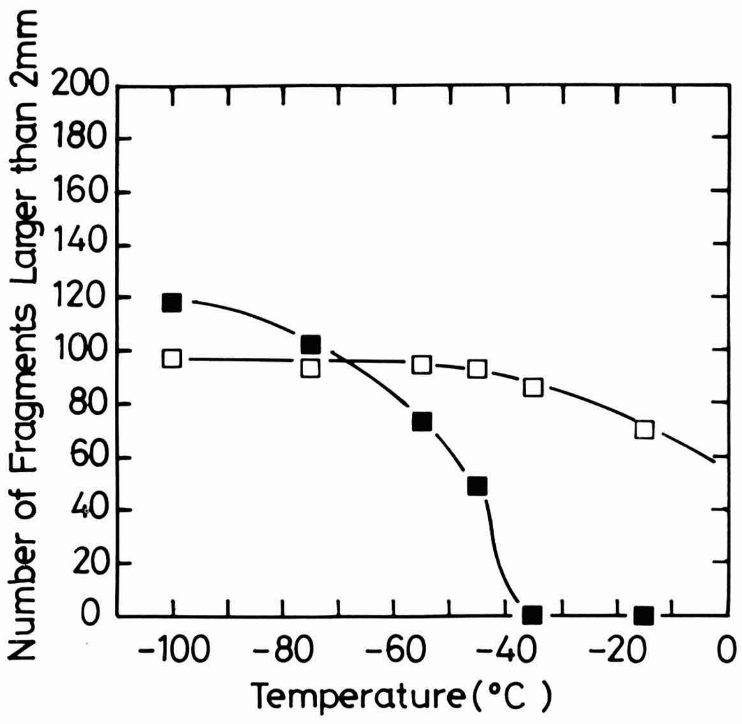

FIG. 6. THE DEPENDENCE OF TEMPERATURE ON THE NUMBER OF FRAGMENTS LARGER THAN 2 mm PRODUCED BY THE IMPACT OF BALL ON ICE CUBE SAMPLES
Pure water ice (□), sweet orange juice ice (■).

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REVERSE OSMOSIS CONCENTRATION OF APPLE JUICE: FLUX AND FLAVOR RETENTION BY CELLULOSE ACETATE AND POLYAMIDE MEMBRANES

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ABSTRACT

Apple juice was concentrated in a pilot scale reverse osmosis unit using two commercial spiral wound cellulose acetate membranes with 97% (CA-97) and 99% (CA-99) NaCl rejection ratings and an experimental polyamide (PA-99) membrane with 99% salt rejection rating. Flux and concentration rates were higher for the PA-99 membrane than for the CA membranes. Gas chromatographic analysis of feed, permeate, and concentrate samples was undertaken and a mass balance of odor-active volatiles was performed. The PA-99 membrane retained 45% of the total odor-active volatiles while the CA-99 retained 23%. Acetates were not found to increase when apple juice was concentrated with the cellulose acetate membrane. Retention of individual aroma compounds for the CA-99 and PA-99 membrane was rationalized using polar, nonpolar, and steric parameters.

INTRODUCTION

Reverse osmosis (RO) occurs when an applied pressure is exerted on the more concentrated solution in excess of the differential osmotic pressure. This causes the solvent (water) to flow from the more concentrated solution to the less concentrated solution.

Osmotic pressure is the measure of the resistance to flow of water through the membrane due to the presence of the solute. It is proportional to solute concentration and varies with the activity and the molecular weight of the solute. In fruit juices, the major contributors to osmotic pressure are sugars (hexoses,

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dissaccharides) and organic acids (Merson and Morgan 1968). Osmotic pressures for fruit juices are about 1.3 MPa (189 psia) to over 10 MPa (1436 psia) for fruit concentrate (MacBean and Smith 1977).

Thijssen (1970), presented an empirical equation for the osmotic pressure of fruit juices:

$$\text{Osmotic pressure (MPa)} = 13.375\ C/(1-C) \qquad (1)$$

where, C is defined as the weight fraction of dissolved solids. Matsuura *et al.* (1973) presented an equation based on the carbon fraction (X_c) in fruit juices and concentrates:

$$\text{Osmotic pressure (MPa)} = (24.546X_c)/(1 - 3.94X_c) \qquad (2)$$

Cross-flow Membrane Filtration

In cross-flow operation, a portion of solvent in the feed, usually water, is forced through the membrane as permeate while unpermeated solutes and solids in solution are carried off with the remainder of the feed in a reduced volume of solution as concentrate. This cross-flow continuous sweeping action minimizes membrane pore blocking and particle buildup, and this allows longer membrane use prior to cleaning (Paulson *et al.* 1984).

Flux Equation

It would be desirable to predict the flux of permeate through a RO membrane. Sourirajan and Matsuura (1977b) have given the flux equation as:

$$N = A[P - \tau(X_{A2}) + \tau(X_{A3})] \qquad (3)$$

where N = solvent flux through membrane; A = permeability constant of membrane; P = operating gauge pressure; τ = osmotic pressure; X_{A2} = concentration of boundary solution at high pressure side; X_{A3} = concentration of permeate. A number of factors influence the flux and the performance of RO membranes: pH, temperature, membrane construction, and concentration polarization.

Preferential Sorption-Capillary Flow (PSCF) Mechanism

A number of mechanisms have been proposed to explain the selectivity of RO membranes for aqueous solutes (Blais 1977). According to the PSCF mechanism, RO occurs due to the preferential sorption of a fluid mixture constituent and fluid permeation through the porous membrane (Sourirajan 1978). The existence of a membrane of the right chemical nature (polar and nonpolar effects) and pores of appropriate size and number (steric effect) are indispensable for RO. The polar parameter measures the extent of the solute's acidity (protondonating characteristic) or basicity (proton-accepting characteristics). The nonpolar parameter quantifies the extent of hydrophobic interactions between the nonpolar part of the membrane and solute. These two factors would influence the composition of the solution at the interfacial layer near the membrane surface.

Separation of Fruit Juice Components

Matsuura *et al.* (1973) discussed the physiochemical criteria for RO separation of fruit juice components using a cellulose acetate membrane. For this purpose, it can be assumed that the major water soluble components in fruit juices consist of 10–20% of sugars, 1% of inorganics, and very small quantities of volatile flavor compounds, vitamins and proteins.

The separation of undissociated alcohols, aldehydes, ketones and esters is governed by the polar effect of the molecule which is described by the Taft number (Sourirajan and Matsuura 1977a):

$$\sigma^* = 1/2.48 \times [\log (k/k_0)_B - \log (k/k_0)_A] \qquad (4)$$

where σ^* = Taft number, k, k_0 = rate constants for hydrolyses of RCOOR′ and CH_3COOR', and B and A refer to respective alkaline and acid hydrolyses carried out for the same R′ under identical experimental conditions. The Taft number is a measure of the electron withdrawing power of the substituent group in a polar molecule. Generally a more negative Taft number results in an increase in the basicity of the molecule and hence higher solute rejection by the cellulose acetate membrane and retention in the concentrate.

An increase in the number of polar functional groups in the acid results in higher preferential sorption for water over the acid. Solute rejection by the membrane decreases in the order: citric (monohydroxy-tricarboxylic acid) > tartaric (dihydroxy-dicarboxylic acid) > malic (monohydroxy-ducarboxylic) > lactic (monohydroxy-monocarboxylic) > acetic, propionic, butyric, valerlic, benzoic (monocarboxylic acids). In the separation of sugars their very high negative Taft number leads to a better rejection by the membrane than all other fruit juice compounds. Each Taft number for a solute corresponds to a critical pore diameter (equal to twice the thickness of the preferentially sorbed interfacial pure water layer) on the membrane surface. There is no necessary correlation between the critical pore diameter and the size of solute and solvent molecules. The critical pore diameter could be larger than either solute or solvent and solute rejection could still take place. The critical pore diameter could also be different for different membrane material-solution systems (Sourirajan 1977).

Thus, the relative separation of fruit juice solutes during RO concentration will depend on the membrane pore size, the relative Taft numbers of water and solute, and the operating conditions of the experiment.

MATERIALS AND METHODS

Preparation of Apple Juice

For experiments with CA-99 membrane, ten bushels each of utility grade Empire and Ida Red apples were purchased from a local vendor in April, 1984. For experiments with PA-99 membrane, 15 bushels of McIntosh apples purchased in July were used. The apples were picked in October 1983 and placed in controlled atmosphere storage until they were purchased.

The apples were comminuted in a hammer mill (W.J. Fitzpatrick Co., Model D, Chicago, IL) and juice was extracted with a hydraulic press (Orchard Equipment and Supply, Model OHP22S, Conway, MA). The juice was depectinized at 48.9 °C(120 °F) with pectinase (Klearzyme 200, G.B. Fermentation Industries, Inc., Charlotte, NC) and filtered in a plate and frame filter press (T. Shriver and Co. Inc., Harrison, NJ).

RO Unit and Its Operation

The depectinized and filtered juice was concentrated with a pilot scale RO unit (Osmonics Inc., Minnetonka, MN). The feed was pumped through the membrane, the permeate was collected, and the concentrate returned to the feed tank. A schematic diagram of the system is shown in Fig. 1.

Two spiral wound membranes: a cellulose acetate (99% salt rejection) (CA-99) membrane and an experimental polyamide (99% salt rejection) (PA99) (Osmonics Inc.) membrane were used. In addition, the unit was operated with another cellulose acetate membrane (97% salt rejection)(CA-97) and data on permeate flux were obtained. The top layer of each membrane consisted of pores in the 5 Angstroms range (Anonymous, no date). Both cellulose acetate membranes had 1.394 m^2 (15 ft^2) membrane area while the PA99 had 0.929 m^2 (10 ft^2) membrane area.

The RO unit was operated with each membrane until the permeate flow rate was very low. The pressure for each membrane was evaluated as the average feed pressure over the entire run while the temperature was evaluated as the average permeate temperature over the entire run. The temperature of the juice was that of the ambient; it ranged from 21.1 to 26.7 °C. The average pressure across each membrane ranged from 4.76 MN/M^2 to 4.85 MN/m^2. At prescribed intervals, 500 mL samples of permeate and concentrate were taken for gas chromatographic analysis of the volatiles. Magnitudes of °Brix, flow rates, feed pump pressure, inlet and outlet of membrane pressures were recorded.

Nonpolar Odor-Active Volatile Analysis

Odor-active volatiles were determined with a gas chromatograph (Model 5840, Hewlett Packard, Palo Alto, CA) as described by Cunningham *et al.* (1986)

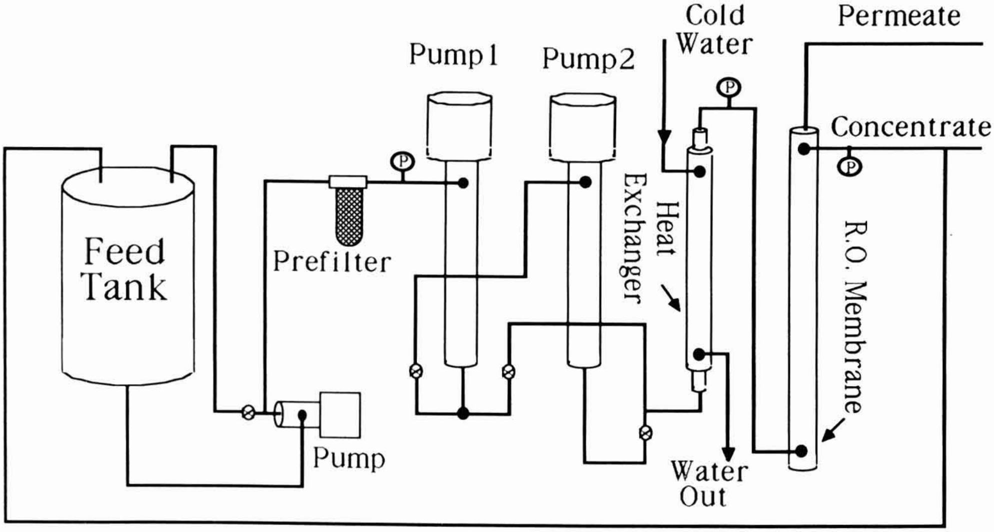


FIG. 1. SCHEMATIC DIAGRAM OF CONCENTRATION OF APPLE JUICE BY REVERSE OSMOSIS

Hydrocarbon Standard. A 1 microliter hydrocarbon standard of carbon 8 to 17 was run through the gas chromatograph. The concentration of C-11 and C-13 was 5 ppm while the other standards were at 20 ppm to better differentiate the peaks. The retention times of these peaks were used together with the unknown sample peaks' retention times to calculate retention indices (RI) for the unknown peaks.

Apple Calibration Standard. A 1 microliter apple calibration mixture consisting of 14 odor-active compounds that have been identified to have important apple aroma and an internal standard of dodecane were run through the gas chromatograph. The compounds, their RI, and their descriptive odors are given in Table 1.

Sample Run. After calibration, 1 mL of concentrated sample was mixed with 1 mL of 2 ppm dodecane. This gave a 2 mL sample with a 1:2 dilution of sample and dodecane. Either 1 microliter of concentrate or 3 microliter of permeate sample from this solution was injected into the GC. The odor-active peaks were identified and their concentrations in ppm were calculated.

TABLE 1.
CALIBRATION MIX OF APPLE ODOR-ACTIVE COMPOUNDS

Compound Name	RI[a]	Descriptive Smell[b]
n-hexanal	780	Fatty, green, grassy
ethyl butyrate	786	Banana, pineapple
butyl acetate	800	Pungent, pear
trans-2-hexenal	827	Green, fruity
ethyl-2-methyl butyrate	838	Green, fruity
isopentyl acetate	865	
propyl butyrate	881	Pineapple, apricot
butyl propanoate (propionate)	889	Fruity, pineapple
pentyl acetate	898	
butyl butyrate	979	Pear, pineapple
hexyl acetate	996	Fruity, floral
butyl pentanoate (valerate)	1078	Apple, raspberry
butyl hexanoate	2180	Pineapple
dodecane (standard)	1200	

[a] adapted from Acree (unpublished) and Jennings and Shibamoto (1980)
[b] adapted from Dimick and Hoskin (1983) and Furia and Bellanca (1971)

DISCUSSION OF RESULTS

Permeate flux

The permeate flux for the cellulose acetate (99% and 97% salt rejection) and the polyamide (99% salt rejection) membranes decreased linearly with increase in °Brix of the concentrate as shown in Fig. 2. Figure 2 also contains the regression equations for the three membranes. Linear relationships were also observed between permeat flux and °Brix of concentrate and between °Brix concentrate and operating time.

Because the operating conditions were nearly the same for the different membranes, one can compare their flux (Merson and Ginnette 1972; Merson *et al.*

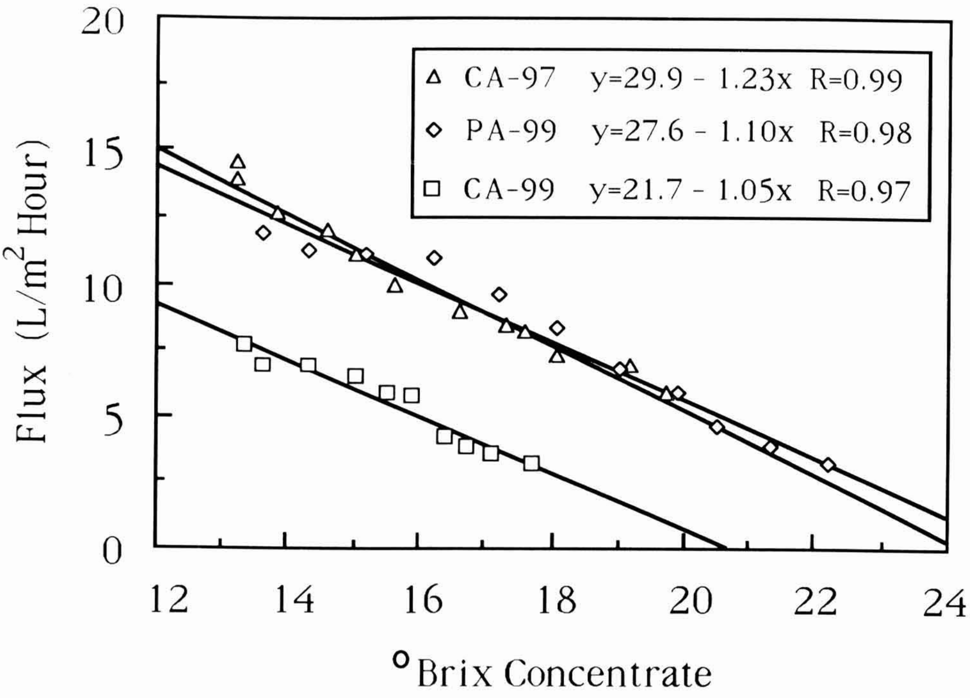


FIG. 2. PERMEATE FLUX AS A FUNCTION OF °BRIX OF CONCENTRATE; CA STANDS FOR CELLULOSE ACETATE AND PA FOR POLYAMIDE

1980). Comparing the CA-97 and CA-99 membranes, the CA-97 had a higher flux over the entire concentration range. This is to be expected because the CA-97 membrane has a lower salt rejection with presumably larger average pore size that allowed for a higher permeate flux. The PA-99 membrane also had a higher flux than the CA-99 over the entire concentration range. These results agree with previous work by Merson *et al.* (1980) who also have reported higher permeate flux for a poly(ester/amide) membrane over a cellulose acetate membrane.

As expected, the flux decreased with time due possibly to an increase in the osmotic pressure at the high pressure side of the membrane, membrane pore blocking by solutes or other macromolecular material and membrane compaction. Practically this means that membranes will need to be cleaned or replaced at specified intervals to maintain an economically justified flux.

ANALYSIS OF GAS CHROMATOGRAPHIC DATA

The gas chromatograph gave the concentration of each identifiable peak in ppm (mg/L) for all the sample extracts. Not all the compounds in the calibration mix were identified. Most of the butyrates were not present because the apples used were subjected to long controlled atmosphere storage. Trans-2-hexenal was probably formed as a product of lipid oxidizing enzyme action on free fatty acids such as linoleic acid. Those compounds that were identified for CA-99 and PA-99 membranes are shown in Fig. 3.

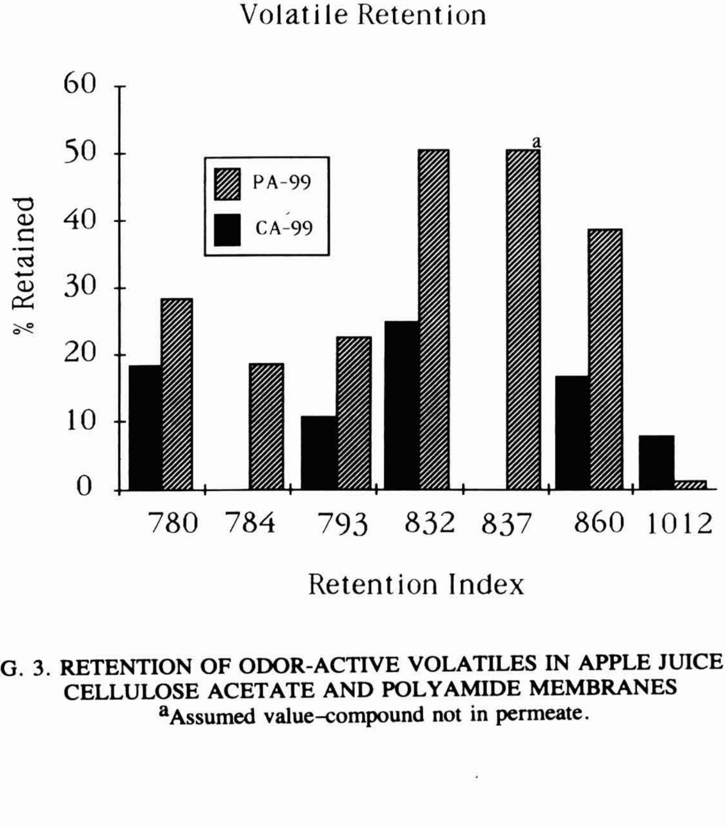


FIG. 3. RETENTION OF ODOR-ACTIVE VOLATILES IN APPLE JUICE BY CELLULOSE ACETATE AND POLYAMIDE MEMBRANES

[a]Assumed value–compound not in permeate.

Mass Balance Equation for Odor-Active Volatiles

A mass balance was done for the individual and total odor-active volatiles as detected by the gas chromatograph. The mass balance equation used was:

$$F = P + C_s + C_f + \text{Loss/Generation} \qquad (6)$$

where F = odor-active volatiles in starting feed, mg; P = odor-active volatiles in permeate stream (including the 500 mL samples), mg; C_s = odor-active volatiles in 500 mL concentrate samples, mg; and C_f = odor-active volatiles left in final concentrate, mg. Assuming the loss/generation to be negligible, the % retention of odor-active odor-active volatiles was defined as:

$$\% \text{ retention} = 100 \times (C_s + C_f)/F \qquad (7)$$

The results of the % retention calculations for the individual odor-active volatiles for the CA-99 and PA-99 membranes are shown in Fig. 3. It should be noted that a portion of the odor-active volatiles was probably lost due to absorption on the membrane, volatilization, mechanical and thermal degradation and other means.

The PA-99 membrane retained 45% of the total odor-active volatiles in the feed while the CA-99 membrane retained 23% of the odor-active volatiles in the feed. The above findings are consistent with Bolin and Salunkhe (1971) who reported a 16% retention of apple odor-active volatiles using a cellulose acetate membrane. These findings also confirm earlier reports by other workers that polyamide membranes do retain more of the polar organic compounds such as aldehydes and acetates than cellulose acetate membranes with about the same average pore size (Blais 1977; Baxter *et al.* 1980; Matsuura *et al.* 1975).

Dickson *et al.* (1975) have reported that the cellulose acetate membrane is more polar than polyamide membrane. A stronger polar membrane would concentrate more of the polar organic solutes at the interfacial layer near the membrane. Thus permeation of the solute rich interfacial layer would lead to lower rejection of polar organic solutes by the cellulose acetate membrane. Conversely, a more hydrophobic and less polar polyamide membrane would show less affinity for polar organic solutes and create a purer interfacial layer. The membrane would thus show a greater rejection of polar organic solutes (Blais 1977). The analysis would be reversed for solutes with predominant hydrophobic character. This does not mean that to reject most polar organic fruit juice components the membrane would repel both solute and solvent (polar water) and require a larger operating pressure to effect separation. A highly hydrophilic membrane would also be undesirable because strong interactions between the membrane and the hydrophilic water would reduce water flux.

This points out the need for the development of membranes with specific properties tailored to meet specific solute rejection characteristics.

Acetates Mass Balance

One concern was that total acetates may increase when apple juice was subjected to RO using a cellulose acetate membrane (i.e. total acetates found in the permeate, concentrate samples and final concentrate are greater than the actual acetates in the initial feed). The results of a mass balance on acetates are:

Total acetates, initial feed = 182.06 mg
Total acetates, permeate stream = 37.64 mg
Total acetates, concentrate samples = 2.84 mg
Total acetates, final concentrate = 25.67 mg

From this calculation, the total acetates (66.15 mg) in the withdrawn permeate, concentrate, and the final concentrate still add up to less than the total acetates in the initial feed (182.06 mg). It is obvious that some acetates were lost due to vaporization, degradation or other means. However, it can be concluded that total acetates did not increase during the RO run of apple juice with cellulose acetate (CA-99) membrane.

REASONS FOR SELECTIVE COMPOUND RETENTION

The retention of the individual compounds ranked as follows:

Retention Ranking	CA-99	PA-99
Highest	trans-2 hexenal	ethyl-2-methyl-butyrate
	n-hexanal	trans-2-hexenal
	isopentyl acetate	isopentyl acetate
		n-hexanal
	butyl acetate	butyl acetate
		ethyl butyrate
Lowest	hexyl acetate	hexyl acetate

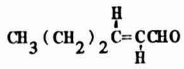
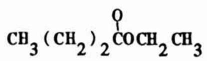
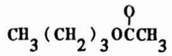
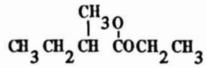
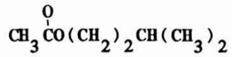
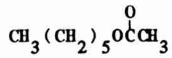
It would be worthwhile now to try to explain why each compound was retained selectively based on the physico-chemical properties. The molecular weights and chemical structures of the detected odor-active volatiles are shown in Table 2.

Based on the molecular weights of the compounds the smallest structure, trans-2-hexenal was retained the most and the largest structure, hexyl acetate was retained the least by the CA-99 membrane. However, RO mechanism is not simply a sieving effect where the molecule larger that the pore would be retained the most. This mechanical sieving effect is true for ultrafiltration and not for RO (in the less than 200 MW range) where a physico-chemical process is the mechanism for solute separation (Hsieh *et al.* 1979).

The extent of solute separation depends on the porosity of the membrane, the nature of the solute functional group, the Taft number for the substituent group and the mass transfer coefficient of solute on the high pressure side of the membrane (Matsuura *et al.* 1973). Generally a more negative Taft number results in higher solute separation. Tabulations of the Taft nos. for the detected odor-active volatiles for the CA-99 and PA-99 membranes are shown in Tables 3 and 4, respectively.

Water has a Taft number of 0.49 which explains its very low rejection and consequently it readily permeates through the membrane.

TABLE 2.
MOLECULAR WEIGHT AND CHEMICAL STRUCTURE OF DETECTED ODOR-ACTIVE VOLATILES[a]

Compound	Cal #	M. W.	Formula	Structure
trans-2 hexenal	5	98.2	$C_6H_{10}O$	 $CH_3(CH_2)_2\overset{H}{C}{=}\underset{H}{C}CHO$
n-hexanal	2	100.2	$C_6H_{12}O$	$CH_3(CH_2)_4CHO$
ethyl butyrate	3	116.2	$C_6H_{12}O_2$	 $CH_3(CH_2)_2\overset{O}{C}OCH_2CH_3$
butyl acetate	4	116.2	$C_6H_{12}O_2$	 $CH_3(CH_2)_3O\overset{O}{C}CH_3$
et-2-me-butyrate	6	130.2	$C_7H_{14}O_2$	 $CH_3CH_2\overset{CH_3}{CH}\overset{O}{C}OCH_2CH_3$
isopentyl acetate	7	130.2	$C_7H_{14}O_2$	 $CH_3\overset{O}{C}O(CH_2)_2CH(CH_3)_2$
hexyl acetate	12	144.2	$C_8H_{16}O_2$	 $CH_3(CH_2)_5O\overset{O}{C}CH_3$

[a]Adapted from Furia and Bellanca (1971) and Jennings and Shibamoto (1980)

TABLE 3.
TAFT NUMBERS OF DETECTED COMPOUNDS IN APPLE JUICE PROCESSED USING CELLULOSE ACETATE-99 MEMBRANE

Compound	MW	% Retention	Taft number[a]
trans-2 hexenal	98.2	25	< -0.133[b]
n-hexenal	100.2	19	-0.133
isopentyl acetate	130.2	18	-0.133
butyl acetate	116.2	12	-0.13
hexyl acetate	144.2	8	-0.134

[a]Adapted from Matsuura *et al.* (1973).

[b]The Taft number was not listed but trans-2-hexenal probably has a more negative Taft number because of its additional double bond compared to n-hexanal. This would probably lead to higher electron density in the double bond and more proton accepting separation.

TABLE 4.
TAFT NUMBERS OF DETECTED COMPOUNDS IN APPLE JUICE PROCESSED USING A POLYAMIDE-99 MEMBRANE

Compound	MW	% Retention	Taft number
Et-2-Me-butyrate	130.2	>>51	-0.310
trans-2-hexenal	98.2	51	-0.133
isopentyl acetate	130.2	39	-0.133
n-hexanal	100.2	29	-0-133
butyl acetate	116.2	23	-0.133
ethyl butyrate	116.2	19	-0.215
hexyl acetate	144.2	1.2	-0.134

Retention by CA-99 Membrane. The cellulose acetate membranes has been said to have both polar and nonpolar character (Sourirajan and Matsuura 1977a). The hydroxyl and oxygen linkages in the cellulose acetate molecule contribute to its polar character and the hydrocarbon group in the ester part of the molecule contribute to its nonpolar character. Further, the cellulose acetate molecule behaves as a net proton acceptor (base). Therefore, a solute which is a proton donor (such as alcohols, phenols, and acids) is attracted to the membrane surface and a solute which is a proton acceptor (such as aldehydes, ketones, ethers, esters and tertiary amines) is repelled from the membrane (Sourirajan 1977). Therefore solute separation may be expected to be influenced by both polar and nonpolar effects.

For the cellulose acetate membrane, it can be seen that the more negative Taft number of trans-2-hexenal resulted in a higher retention. The Taft nos. for n-hexanal, isopentyl acetate, butyl acetate and hexyl acetate are about equal. Since the Taft number represents the polar effect of the substituent group only, the total polar effect of the molecule is different for different functional groups at a given Taft number. This explains that even compounds with the same Taft number can have different solute rejection.

Hexyl acetate was the highest molecular weight compound with the longest hydrocarbon chain. This hydrocarbon chain being nonpolar in character would probably be attracted to the hydrophobic part of the cellulose acetate membrane and thus hexyl acetate would be more preferentially sorbed and permeated than any of the other lower hydrocarbon chain length compounds. Thus the nonpolar effect would be more significant in the longer hydrocarbon length compounds. This points out the significance of both polar and nonpolar effects in influencing solute rejection.

Retention by PA-99 Membrane. Broadly speaking, the polyamide membranes have an amidic nitrogen $-\overset{H}{N}-\overset{O}{C}-$ in this characteristic polymer linkage which retains a labile proton and an uncoupled share of electrons. Under acidic conditions, polyamide can protonate to $-\underset{H}{\overset{H+}{N}}-\overset{O}{C}-$ and acquire a protoelectrolyte character (Blais 1977).

Matsuura *et al.* (1975) and Dickson *et al.* (1975) have pointed out that the polyamide membrane is more nonpolar than cellulose acetate and that the polyamide membranes appear to act as an acid with a net positive charge while that of cellulose acetate appear to act as a base with a net negative charge.

As with solute separation of cellulose acetate membranes, the more negative the value of the solute Taft number, the greater the solute rejection of polyamide membranes. This has been shown with polyamide membranes experimentally for alcohols by Matsuura *et al.* (1975) and for alcohols, ethers, ketones, and aldehydes by Dickson *et al.* (1975).

From Table 4, the most negative Taft number of ethyl-2-methyl-butyrate with a Taft number of −0.310 was retained the most at greater than 51% retention. Trans-2-hexenal was the second most retained compound due to its having a more negative Taft number than isopentyl acetate, n-hexanal, butyl acetate or hexyl acetate. However, ethyl butyrate with a Taft number of −0.215 had a relatively low retention. Based on the Taft number it should have been the second most retained compound after ethyl-2-methyl-butyrate. This does not mean that the criterion of more negative Taft number resulting in higher solute rejection does not work. Assuming that the gas chromatograph correctly identified this compound, its low retention in the concentrate could mean that it was lost by possible adsorption on the membrane, thermal or mechanical degradation or being evaporated much more easily into the atmosphere.

The above rationale for polyamide membrane solute separation does not seem to be valid if consideration is given only to polar effects. This means that since the polyamide membrane has a reported acidic character of net positive charge, a more negative Taft number results in a more basic character. This would reverse the solute rejection rationale because a more negative Taft number would lead to not greater but less solute rejection due to attraction of the more basic solute with the more acidic polyamide membrane. This would seem to point out that nonpolar, steric and other parameters may be more important than the polar effect in determining solute rejection in polyamide membranes.

Thus, the Taft number criterion for solute separation worked well for the cellulose acetate membrane for which the original physico-chemical data were based on. Further studies need to be made to determine physico-chemical criteria for both solute and membrane in order to predict solute rejection characteristics of the different membranes.

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