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IMPROVED METHOD FOR PREPARATION OF FRUIT-SIMULATING ALGINATE GELS

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ABSTRACT

Calcium binding, crosslinking, and mechanical properties were studied in alginate gels prepared by a two-step procedure. A thermolabile gelatin gel containing sodium alginate is placed in a calcium lactate solution, and diffusion of calcium ions causes crosslinking of the alginate. Calcium binds completely to alginate within 48 h, but crosslinking continues for more than 72 h, as indicated by gel strength.

Retention of ascorbic acid incorporated into these gels was only about 25% after 72 h in the crosslinking bath. To improve retention, an alternate one-step procedure was adopted, using glucono-delta-lactone (GDL) and dicalcium phosphate dihydrate; this process eliminates residence in the crosslinking bath. Hydrolysis of GDL slowly reduces the mixture's pH, releasing calcium ions which then crosslink with the alginate. The GDL process produced a gel matrix with compression behavior similar to those of the "two-step" gels. Complete crosslinking took 7 h; ascorbic acid losses were insignificant.

INTRODUCTION

Alginic acid and its salts have been widely accepted and used in foods for many years (McDowell 1975). One particularly useful property of alginates is their ability to crosslink with divalent ions, especially calcium, to form a matrix with excellent water-holding capacity and rheological behavior which can be modified to simulate that of natural fruits (Haug *et al.* 1967; Kohn *et al.* 1968; Rees 1972; McDowell 1974).

Various methods have been used to develop a fabricated fruit product based on such an alginate matrix. Szczesniak (1968) showed that nonuniform cellular structures simulating fruits and vegetables can be prepared by diffusing certain alkaline earth metal salts into alginate solutions. In some cases, fruit puree or fruit pulp has been incorporated

into the simulated fruit preparation (Luh *et al.* 1977). A patent was issued (Wood *et al.* 1974) in which encapsulated fruit is formed by incorporating dissolved calcium or aluminum ions in the edible materials and forming drops or small portions. These drops are brought into contact with an alginate or pectate sol, forming a calcium or aluminum alginate skin around the drop. Another patent (Sneath 1975) uses an encapsulation process in which drops are formed by extrusion, coated with alginate or pectate sol, and treated in a setting bath of calcium ions.

In the two-step gelation procedure of Luh *et al.* (Anonymous 1977; Luh *et al.* 1976), a gelatin-containing alginate mixture is chilled to obtain a soft gelatin gel, which is then placed in a crosslinking bath to form calcium alginate.

The delicate texture of fruits or simulated fruit systems usually cannot sustain freezing or freeze-drying treatments, becoming either spongy or rubbery after thawing or rehydration. Compounds of high water-holding capacity, including pectin and sucrose, can, however, be incorporated to improve textural quality. The simulated products have a long shelf life, the labile components being the flavor and nutrients.

The present study started with the two-step system of Luh *et al.* (1976, 1977), which consisted of sodium alginate, gelatin, pectin, sucrose, and calcium ions. Slow diffusion from the calcium lactate bath to the gel pieces, however, was not favorable for retention of water-soluble components such as sucrose and vitamins (especially ascorbic acid). Therefore, a system more favorable for retention of water-soluble constituents was used (McDowell 1974). In this one-step system, glucono-delta-lactone (GDL) is hydrolyzed slowly, lowering the system's pH enough to release calcium ions and allow crosslinking. This system was modified further in an attempt to simulate properties of both fresh and processed gels prepared by the two-step system.

The goal of this study was to develop a gel with the textural qualities attainable by the two-step process, while improving the gel formation process and maintaining high retention of water-soluble nutrients.

MATERIALS AND METHODS

Preparation of Gels Using a Two-Step Gelation Procedure

To produce a 2.5% alginate-2.0% gelatin gel, 4.0 g gelatin (Knox Gelatin, Inc., Englewood Cliffs, NJ) were weighed and dissolved in 200 ml distilled water while stirring on a hot plate, and poured (while still warm) into a Waring blender. With the blender at low speed, 5.0 g sodium alginate (Kelco Gel LV, KGLV-2457-52; Kelco Co., San

Diego, CA) were added gradually. After the alginate was dissolved, the blender was operated at high speed for 30 s. The homogenized mixture was then poured into preweighed small petri dishes (3.5 cm diameter x 1 cm height) and refrigerated until firm (about 4 h).

A 4.5% (w/v) calcium lactate (5-hydrate, U.S.P.-F.C.C., food grade; J.T. Baker Chemical Co., Phillipsburg, NJ) solution was prepared. The petri dishes containing the alginate gel were immersed in this solution and refrigerated until crosslinking was complete.

Analysis of Calcium in Crosslinked Gels

Total Calcium Determination. Pulverized, freeze-dried gel (1.20 g) was ashed in crucibles for 4-5 h at 525°C. Concentrated HCl was added until no further reaction was noted (CaO + HCl causes violent fizzing). The sample was transferred carefully to a 100-ml volumetric flask and diluted to volume with distilled water. A volumetric portion of sample was titrated with EDTA, using Eriochrome Black T as indicator for analysis of calcium.

Analysis of Unbound Calcium. Three whole freeze-dried gels (removed from petri dishes) were placed in a flask, and 150 ml distilled water were added. The flask was sealed and the samples were shaken for 72 h. Samples were filtered through coarse filter paper (#589 Black Ribbon; Schleicher and Schuell, Inc., Keene, NH). A volumetric portion of clear filtrate was analyzed by titration with EDTA.

Analysis of Bound Calcium. The samples used in the unbound calcium extraction were blotted dry to remove excess solution from the surface. The samples were then re-freeze-dried, ashed, and titrated with EDTA.

Freeze-drying of the Gels. Gels, still in petri dishes, were covered and frozen overnight. Liquid N_2 was poured over the gels to prevent thawing during the initial stages of freeze-drying. The gels in petri dishes were then placed on a tray in the freeze-drier and left for 48-72 h. After freeze-drying, the gels were removed and stored in a desiccator.

Titration with EDTA. EDTA solution was prepared by weighing 8.0 g EDTA (Fisher Scientific Co., Fair Lawn, NJ) and 0.2 g $MgCl_2 \cdot 6H_2O$ (Baker) into a 2-liter volumetric flask. Distilled water was added to volume.

Standard $CaCl_2$ solution was prepared by weighing 0.4 g of primary standard (dried) $CaCO_3$ (Mallinckrodt Chemical Works, St. Louis, MO) into a 500-ml volumetric flask. About 200 ml of distilled water were added; then 6 N HCl (Baker) was added dropwise until cloudiness

disappeared. The solution was then diluted to volume with distilled water.

Buffer was prepared by dissolving about 67.5 g ammonium chloride (Baker) in 570 ml ammonium hydroxide (Fisher) and diluting to 1000 ml with distilled water (pH - 10).

EDTA was standardized by placing 50-ml volumetric portions of $CaCl_2$ solution in three 250-ml Erlenmeyer flasks. Five milliliters of buffer were added to each flask. About 6 drops of Eriochrome Black T (Fisher) indicator solution were added to each sample, and samples were mixed by swirling. Samples were titrated with EDTA until the red color changed to blue (38-40 ml). Gel samples were titrated similarly.

Compression Behavior of Gels

The compression conditions of the Instron Universal Testing Machine were: crosshead speed = 20 mm/min; chart speed = 500 mm/min. The instrument was set to perform one full cycle of compression, i.e., to compress the gel once and return to its original position. The load cell used was 500 kg capacity; the cycle was set to move a constant distance before returning, so that the percentage of deformation ($\Delta L/L_o \times 100$) varied slightly with each gel, depending on its height, although each gel was about 1 cm high.

The gel was removed from the petri dish with a spatula. Its height and diameter were measured with a micrometer and recorded. The gel was then placed on the load cell and the compression cycle started. The chart plots stress (S) versus strain ($\Delta L/L_O$). The gels were compressed to 20-25% of their original height. The gels usually ruptured between strains of 0.5 and 0.7.

$$S = F/A \quad (kg/cm^2)$$

$$\Delta L/L_O = \text{strain}$$

L_o = original height of gel (mm)
ΔL = distance of deformation of gel (mm)
A = initial surface area of the gel (cm^2)
F = force of compression (kg)

Ascorbic Acid Determination in Alginate Gels

L-Ascorbic acid (1.5 g; General Biochemicals, Chagrin Falls, OH) was added to the gelatin-alginate mixture after the alginate was dissolved. This mixture was protected from light and air and allowed to set in petri dishes until firm at 6°C. The gels were then frozen, freeze-dried in the dark, and stored in a desiccator at 6°C and protected from light until analyzed for ascorbic acid.

Ascorbic acid content was determined using the indophenol method, as described in the AOAC Official Methods of Analysis (Horwitz *et al.* 1975). Samples from freeze-dried gels were obtained as follows: a portion of freeze-dried gel (about 4 g) was rehydrated for 10 min in 40 ml H_2O, 60 ml of HPO_3-HOAC-H_2SO_4 were added, and the solution was homogenized for 10 min at high speed in a Waring blender. The mixture sat until a liquid formed on the bottom of the container. One-milliliter portions of this liquid were used in the indophenol titrations.

Preparation of Gels by Reduction of pH

By using a slow-releasing acid or a substance that slowly reduces the pH of the alginate mixture, it is possible to add a calcium source that is soluble at lower pH's at the same time as the other components, thus eliminating the crosslinking bath. In this study, three different systems were used, the proportions and amounts of the ingredients being manipulated to obtain stronger gels. The strongest 2.5% (w/v) alginate gels resulting from each of the systems were:

System I:

Sodium alginate	5.0 g
Calcium citrate (200 mesh)	2.0 g
Water	200 ml

The alginate was dissolved in three-quarters of the water, and the calcium citrate (Pfaltz and Bauer, Inc., Stamford, CT) was slurried in the rest. The slurry was added to the alginate solution, mixed thoroughly, and immediately poured into molds, covered, and refrigerated.

System II:

Sodium alginate	5.0 g
Dicalcium phosphate dihydrate ($CaHPO_4 \cdot 2H_2O$)	2.44 g

Glucono-delta-lactone (GDL)	5.04 g
Water	200 ml

The alginate was dissolved in about three-quarters of the water. The GDL (Eastman Kodak Co., Rochester, NY) was dissolved in the remainder of the cold water and the dicalcium phosphate (N.F.-F.C.C., food grade; Baker) was slurried into this solution, which was then mixed into the alginate solution, and poured immediately into molds, covered, and refrigerated.

System III:

Sodium alginate	5.0 g
Dicalcium phosphate anhydrous ($CaHPO_4$)	1.4 g
Adipic acid	2.0 g
Water	200 ml

The alginate and dicalcium phosphate (Mallinckrodt, Inc., St. Louis, MO) were mixed. The mixed powder was stirred in about three-quarters of the water. When the alginate had dissolved, the adipic acid (Matheson, Coleman, and Bell, Norwood, OH) was slurried in the remainder of the water. This slurry was added to the suspension of calcium phosphate in the alginate solution and mixed thoroughly. It was poured immediately into molds, covered, and refrigerated.

Addition of Components Not Directly Involved in Crosslinking

Additional components were added to some GDL gel formulations after alginate was dissolved in the water: sucrose (Domino Sugar, Amstar Corp., New York, NY), 0, 15, or 30 g/100 ml H_2O; gelatin or Avicel (microcrystalline cellulose; FMC Corp., Marcus Hook, PA), 0 or 2.5% (w/v).

Freeze-Drying/Rehydration and Freezing/Thawing of Gels

GDL gels were made and allowed to crosslink at room temperature. Gels were (a) not treated; (b) placed in the freezer 0, 3, or 6 h after formulation, frozen overnight, thawed overnight at 6°C, and held at room temperature for 3 h; or (c) placed in the freezer 0, 3, or 6 h after formulation, frozen overnight, freeze-dried, and rehydrated for 3 h. The untreated samples (a) were tested on the Instron at various

intervals up to about 10 h. Treated samples (b and c) were tested on the Instron after their respective treatments.

RESULTS AND DISCUSSION

The objectives of this investigation were: (1) To study the relations between time of crosslinking, calcium binding, and mechanical properties of an alginate gel capable of being frozen, freeze-dried, and rehydrated; (2) To study the feasibility of incorporation of water-soluble nutrients in the alginate gel, using ascorbic acid as the model nutrient; (3) To modify the crosslinking procedures to minimize process time and maximize nutrient retention.

Binding of Calcium and Its Relation to Crosslinking

Gels used in this study were made using the two-step procedure of Luh *et al.* (1977). The gels were tested after crosslinking for 66 h in a calcium lactate solution. The gels were either "constant gelatin" (gelatin concentration was 2% and alginate concentration varied from 2.0 to 3.5%) or "constant polymer" gels (both alginate and gelatin were varied so that their total concentration in the gel was 5.5% [alginate + gelatin = 5.5%]).

In "constant gelatin" gels, the bound calcium remains fairly constant at 108 ± 6 mg Ca^{++} /g alginate, decreasing only slightly as alginate concentration is increased. For "constant polymer" gels (Fig. 1), bound calcium per gram alginate decreases drastically as alginate concentration increases. One reason for this behavior may be closer packing of alginate chains as the gelatin concentration decreases. Close packing itself may retard diffusion of calcium into the gel, but initial crosslinking of these closely packed chains is probably another major cause of such retardation. In another experiment, "constant gelatin" gels were crosslinked for only 48 h. Bound calcium was constant at 109 ± 8 mg Ca^{++} /g alginate (the same level as after 66 h), while both total and surface calcium per gram alginate decreased. This could indicate that these gels are totally crosslinked within 48 h, or at least that binding of calcium ions to alginate is complete within this time (Fig. 2).

Compression tests were performed on constant gelatin gels using the Instron Universal Testing Machine, and stress-strain curves were determined as a function of alginate concentration. As the alginate concentration is increased, both stress at a given strain and bound calcium per sample are increased. Bound calcium is directly related to the

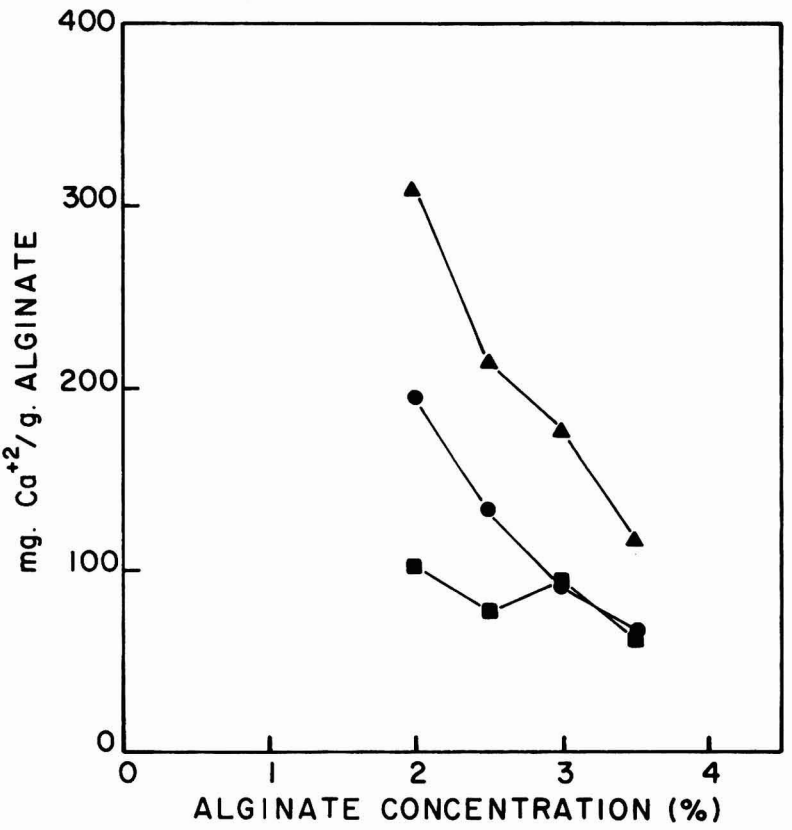

FIG. 1. TOTAL, SURFACE, AND BOUND CALCIUM PER GRAM ALGINATE AS A FUNCTION OF ALGINATE CONCENTRATION (66 h CROSSLINKING, "CONSTANT POLYMER" GELS)
▲—▲, Total; ●—●, Bound; ■—■, Surface.

gels' stress, and thus strength. Therefore, the higher the alginate concentration, the greater the degree of crosslinking, as demonstrated by compression strength of the gels. Total calcium per sample also correlates with stress, because of the relationship between total and bound calcium. If the total calcium in the gel is sufficient, the bound calcium per gram alginate will remain constant. If the total calcium diffusion into the gel is greatly inhibited, the amount of calcium bound to the alginate will also be reduced greatly.

Compression behavior of both "constant gelatin" and "constant polymer" gels was studied as a function of time of crosslinking. In both cases, calcium binding appears to be complete after about 40 h, but the gels' strength continues to increase even up to 90-100 h.

There was a direct relationship between alginate concentration and stress at a given strain, for "constant polymer" gels (Fig. 3). However, for gels with a given alginate concentration, increasing the gelatin concentration caused a lower stress at a given strain. Gelatin molecules may retard crosslinking of alginate chains by separating them physically.

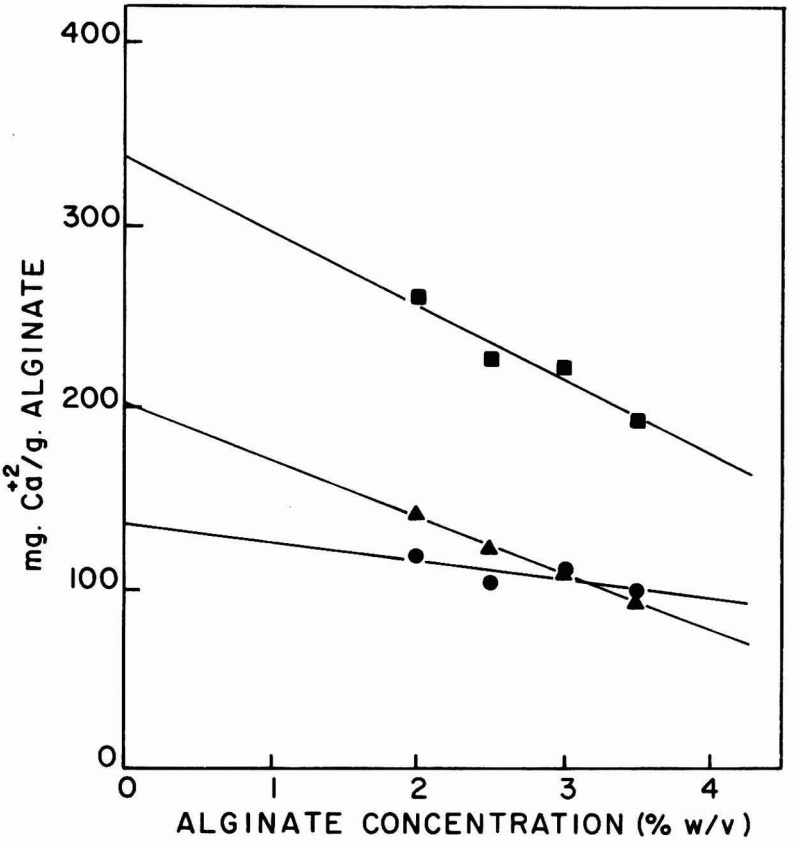

FIG. 2. TOTAL, SURFACE, AND BOUND CALCIUM PER GRAM ALGINATE AS A FUNCTION OF ALGINATE CONCENTRATION (48 h CROSSLINKING, "CONSTANT GELATIN" GELS)

■—■, Total; ▲—▲, Surface; ●—●, Bound.

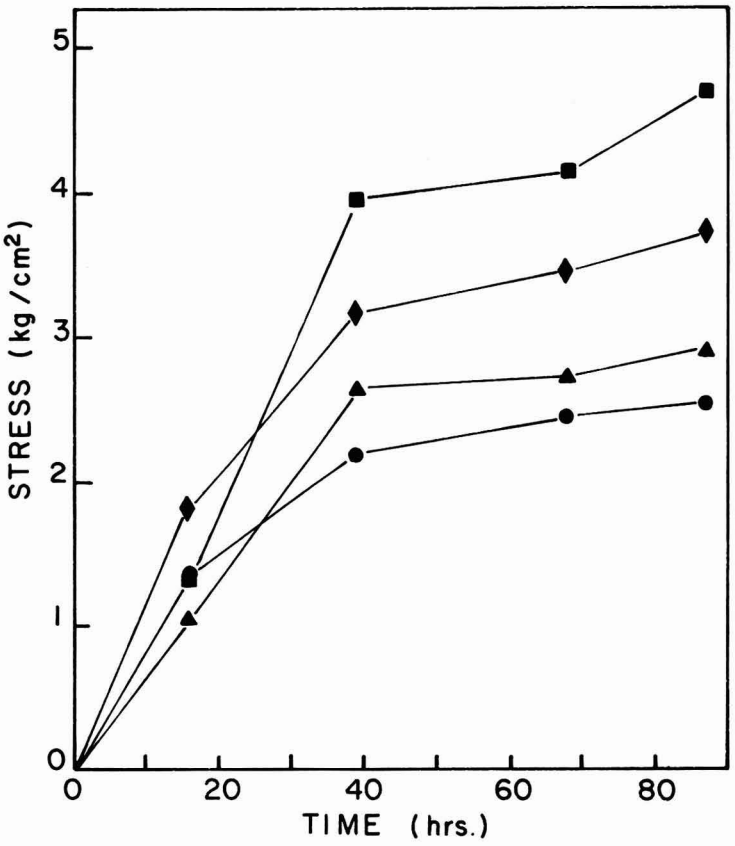

FIG. 3 STRESS (AT STRAIN = 0.5) VS. CROSSLINKING TIME OF "CONSTANT POLYMER" GELS AS A FUNCTION OF ALGINATE CONCENTRATION

●—● = 2.0% Alginate, 3.5% Gelatin; ▲—▲ = 2.5% Alginate, 3.0% Gelatin; ◆—◆ = 3.0% Alginate, 2.5% Gelatin; ■—■ = 3.5% Alginate, 2.0% Gelatin.

In summary, calcium analysis showed that binding of ions (but not necessarily crosslinking) is complete within 48 h. However, compression tests showed that gel strength continues to increase for up to at least 90 h, although at a rate much lower than the initial rate. Since no syneresis was observed, the increase in gel strength apparently is caused by an increase in crosslinking. Crosslinking, as indicated by gel strength, is nearly complete at 68 h. Thus, ion binding cannot be used to measure complete crosslinking of alginate. Perhaps calcium is bound

to the maximum available sites by 48 h, but longer times allow more chains to come into contact, thus allowing more crosslinks to be formed, or perhaps longer times allow already existing crosslinks to be strengthened, by increasing the number of contiguous crosslinked units in a given junction zone. This hypothesis agrees with present theories of crosslinking of alginate by calcium. Our results suggest that crosslinking occurs mostly with polyguluronic acid blocks, although some calcium also binds to polymannuronic acid blocks and alternating mannuronic-guluronic acid blocks.

Luh *et al.* (1976) proposed, on the basis of visual estimation of rate of advance of the "gel-sol" boundary, that crosslinking time is given by:

$$t = kd^2$$

d = one half the shortest dimension (cm)
t = time (min)
k = constant dependent on the gel's composition and crosslinking conditions.

According to this equation, the gels used in this investigation should have crosslinked completely in 24 h. However, compression studies showed that gels were very weak after this time. Apparently, the time determined by the equation of Luh *et al.* (1976) applies only to the time of initiation of crosslinking in a given location, but not to the time at which maximum gel strength is achieved. Since gel strength is related to the amount of crosslinked calcium, we propose that gel strength, as measured by Instron tests, more closely approximates the time necessary for complete crosslinking of the gels.

Ascorbic Acid Retention in Gels

The gel formation process causes extensive losses of incorporated nutrients, especially water-soluble vitamins (Luh *et al.* 1977). Ascorbic acid was incorporated in the aqueous phase before crosslinking and in the crosslinking bath to prevent diffusion from the gel. Most of the incorporated ascorbic acid was retained physically by the gel, but the neutral pH of the crosslinking medium rendered ascorbic acid unstable, resulting in very low retentions after freeze-drying of the gels.

In the present studies, retention of ascorbic acid in calcium lactate gels during gel formation was reduced most extensively by exposure to the crosslinking bath, losses being due to leaching and destruction caused by oxygen and the neutral pH of the bath. After 72 h of crosslinking, only 25% of the ascorbic acid remained (Fig. 4). GDL gels con-

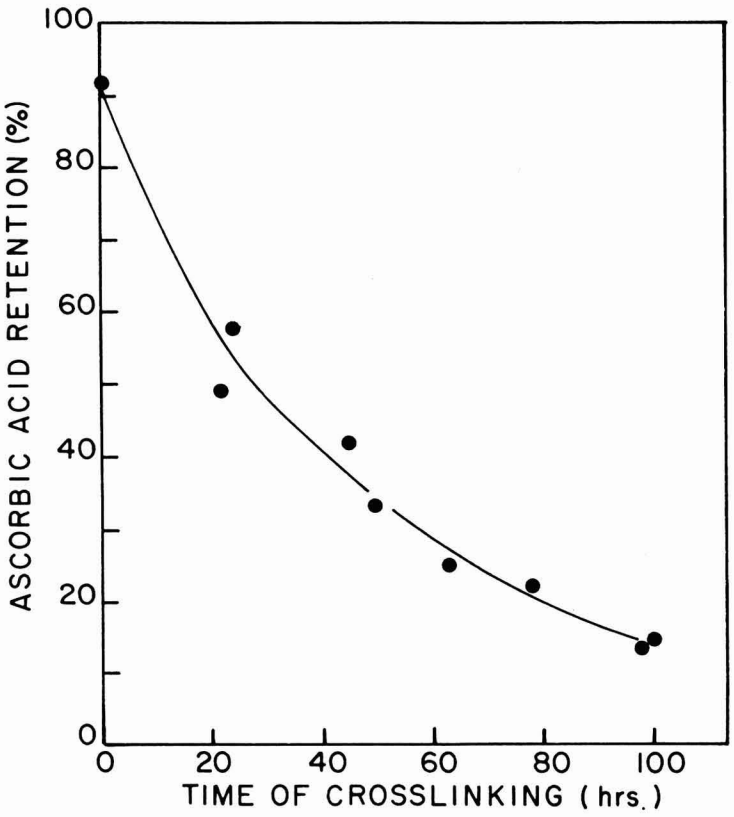

FIG. 4. EFFECT OF TIME OF CROSSLINKING IN 4.5% CALCIUM LACTATE BATH ON ASCORBIC ACID RETENTION BY GELS

taining 30% sucrose and 2.5% gelatin retained 98.9 ± 0.3% ascorbic acid.

Gel Formation by Reduction of pH

To improve the retention of water-soluble vitamins, crosslinking in the bath was eliminated and the calcium ions were introduced simultaneously with the alginate and other ingredients. Thus gelatin was no longer needed to provide rigidity during crosslinking in the bath to maintain the desired final shape of the gel pieces.

The pH of the alginate-water solution was near neutrality. Thus, addition of calcium sources that are soluble at neutral pH immediately released calcium ions, causing immediate crosslinking. This reaction occurred within a few seconds, mixing was incomplete and the result-

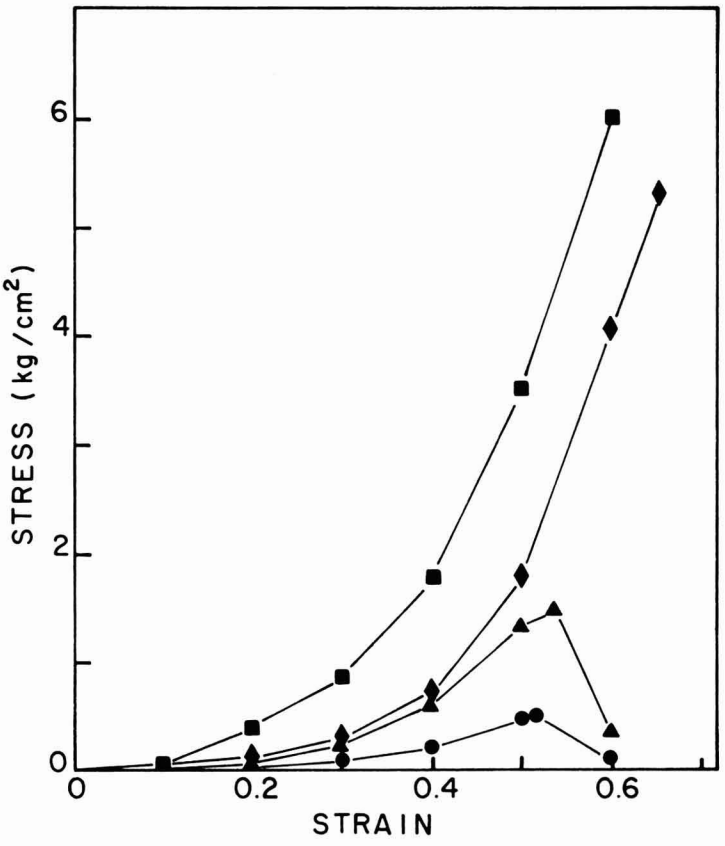

FIG. 5. COMPARISON OF STRESS-STRAIN CURVES OF 2.5% ALGINATE GELS

Best gels of each acidic system after 72 h of crosslinking. Calcium lactate gel after 68 h of crosslinking.
●—●, Calcium citrate; ▲—▲, Adipic acid; ◆—◆, GDL; ■—■, Calcium lactate.

ing gels very inhomogeneous.

If a calcium compound that is soluble at a lower pH is used in conjunction with some "slow-releasing" acid, the solution's pH decreases slowly, allowing complete mixing as well as shaping into a desired form before enough calcium ions are released to form a solid gel. Several such systems have been developed. Our goal was to form a gel with mechanical strength and textural properties similar to those of the gels crosslinked in the calcium lactate bath.

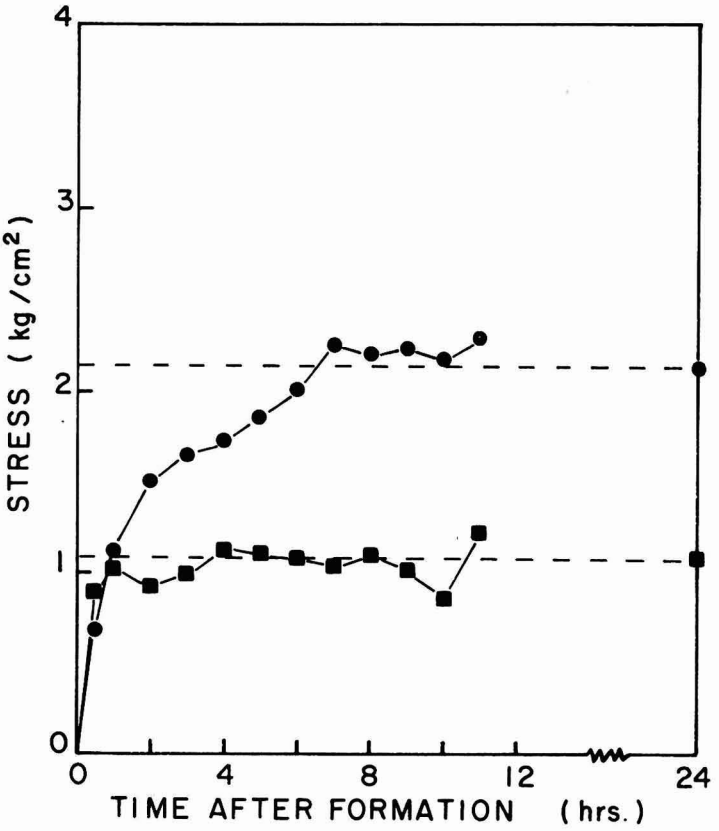

FIG. 6. STRESS (AT STRAIN = 0.5) OF BOTH GDL AND ADIPIC ACID GELS DURING THE FIRST 12 h AFTER FORMATION
■—■, Adipic acid; ●—●, GDL.

The systems chosen (described in MATERIALS AND METHODS) were manipulated to produce the strongest possible gels. The final gels had the following breaking strengths (maximum stress), in kg/cm^2: system I, 0.56; system II, 5.31; system III, 1.66; calcium lactate, 6.5-7.0. Fig. 5 shows the stress-strain curves of these gels.

The best system was that using GDL and dicalcium phosphate dihydrate. For these gels, crosslinking was complete after 7 h. Syneresis began after about 2 h. With the system using adipic acid and anhydrous dicalcium phosphate, crosslinking was complete after 4 h, but these gels were much weaker than GDL gels (Fig. 6). Incorporation of adipic

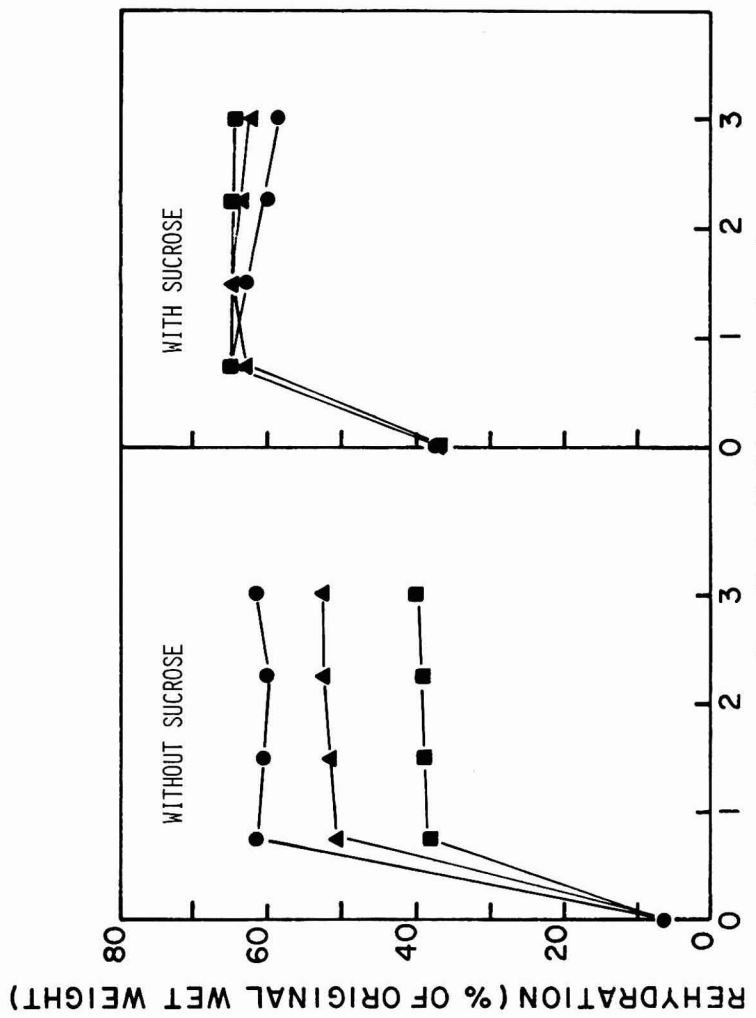

FIG. 7. REHYDRATION (EXPRESSED AS % ORIGINAL WET WEIGHT) OF FREEZE-DRIED GDL GELS, WITH OR WITHOUT SUCROSE, AS A FUNCTION OF REHYDRATION TIME

Time before freezing: ●—●, 0 h; ▲—▲, 3 h; ■—■, 5.5 h.

acid into the GDL system not only did not improve crosslinking time, but weakened the gels.

Effects of Freeze-Drying/Rehydration or Freezing/Thawing on Compression Behavior of Alginate Gels

Both freeze-drying and freeze/thawing weakened GDL and calcium lactate gels, especially when the gels did not contain sucrose, Avicel, or other additives.

Effects of Added Components on Compression Behavior of Alginate Gels

One distinctive feature of gels prepared with slowly releasing acids is that several hours after formation, syneresis starts, shrinking the gels and releasing free water. This syneresis can affect both crosslinking and compression behavior. The decrease in volume promotes crosslinking of the alginate chains because of closer contact, and produces harder or more brittle gels by reducing the water-filled space between the alginate chains. It is difficult to ascertain the relative magnitude of these two effects since both increase gel strength during compression.

When sucrose is added to an alginate system, a longer crosslinking time is needed (Luh *et al.* 1977). Sucrose-containing gels showed a higher stability to freeze-drying. In compression tests, sucrose decreased gel strength. Sucrose, when incorporated into the GDL gels, reduced gel strength only slightly. It was predicted that sucrose incorporation might be used not only to stabilize the GDL gels during freeze-drying, but also to reduce syneresis and thus water loss and shrinkage. This prediction was tested both by measurement of shrinkage of fresh gels and by rehydration behavior of freeze-dried gels.

Shrinkage of sucrose-containing gels was significantly reduced, if not totally eliminated, compared to nonsucrose-containing gels. Gels were made either with or without sucrose, and placed in the freezer at 0, 3, or 5.5 h after formation. Frozen gels were then freeze-dried and rehydrated. Rehydration time for all gels was less than ¾ h, although the exact time was not determined (Fig. 7). Syneresis affects rehydration behavior of gels without sucrose. When the time between formation and placing in the freezer is increased, gels shrink more and become compact, thus reducing their rehydratability. In gels with 45.5% sucrose, syneresis seems totally eliminated; all gels, no matter when they are placed in the freezer, rehydrate to the same level.

Sucrose-containing gels lose weight during immersion in the rehydration bath. This effect is more marked in gels frozen soon after formation, and presumably before completion of crosslinking. The more-crosslinked structure inhibits the sucrose leaching to a greater degree than does the less-crosslinked structure.

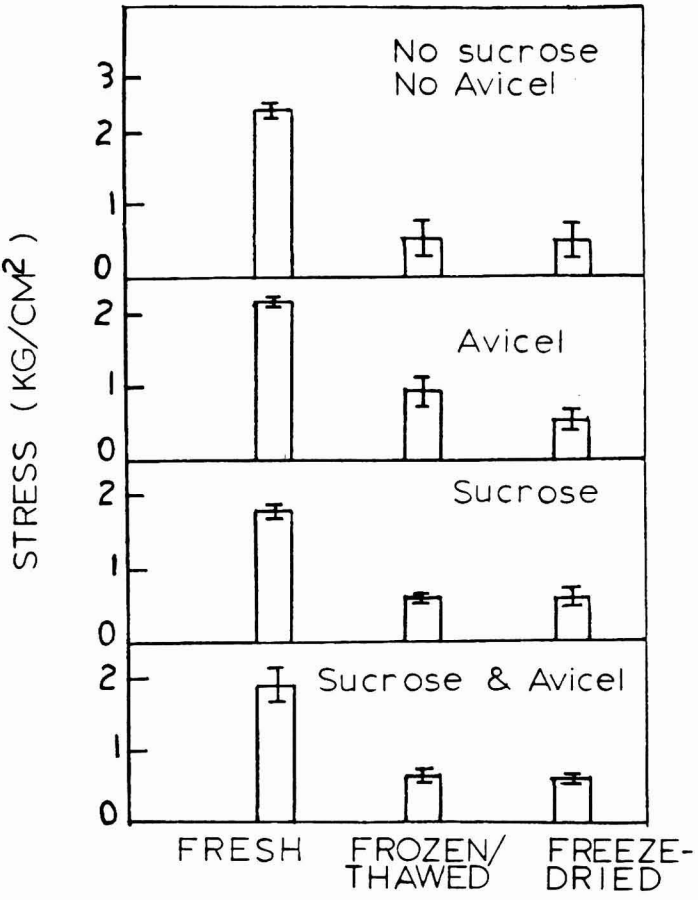

FIG. 8. EFFECT OF PROCESSING ON STRESS (AT STRAIN =0.5) FOR CALCIUM LACTATE GELS IN PRESENCE AND ABSENCE OF ADDITIVES

When incorporated into GDL gels, microcrystalline cellulose (Avicel) weakens gels without sucrose and strengthens gels with sucrose. Sucrose weakens all gels, with or without Avicel. Sucrose interrupts the regularity between alginate chains and thus decreases crosslink formation between chains and/or decreases the size of the junction zones formed. Avicel also interferes with junction zone formation.

Avicel had almost no effect on the strength of processed GDL gels. Sucrose, although it weakens the strength of fresh gels, strengthens processed gels slightly. Effects of freezing and thawing, and of freeze-drying, on calcium lactate gels were also studied, in the presence and

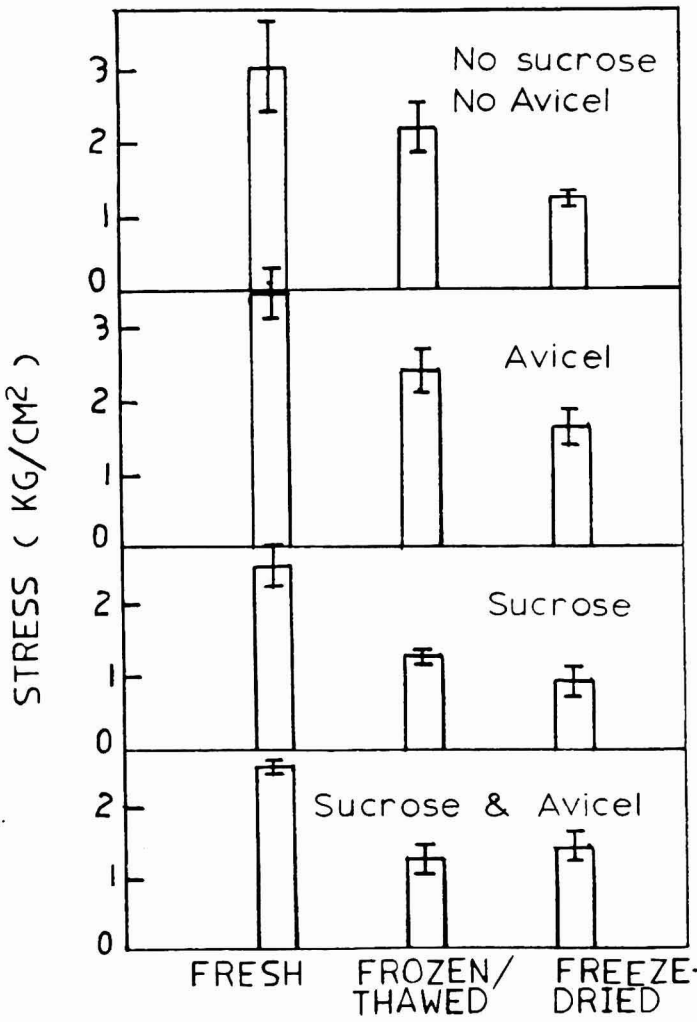

FIG. 9. EFFECT OF PROCESSING ON STRESS (AT STRAIN =0.5) FOR GDL GELS IN PRESENCE AND ABSENCE OF ADDITIVES

absence of additives. Sucrose reduced the initial rate of crosslinking, increased gel sensitivity to freezing and thawing, and decreased the sensitivity to freeze-drying (Fig. 8).

Sucrose only slightly weakened fresh gels, extensively weakened gels that were frozen and thawed, but strengthened freeze-dried gels. Figure 9 presents similar results for GDL gels. Their compressive

strengths were lower after processing than those of comparable calcium lactate gels.

CONCLUSIONS

A system containing sodium alginate, water, GDL, dicalcium phosphate dihydrate, and sucrose can form a gel matrix that has compressive strength similar to that of calcium lactate gels before processing, but significantly lower after processing. They were, however, judged acceptable. Crosslinking time is 7 h in the GDL gels, but it is at least 72 h for calcium lactate gels. The one-step crosslinking process is much more convenient than the two-step procedure used for calcium lactate gels, and improves retention of water-soluble nutrients.

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IMPROVEMENT OF ORGANOLEPTIC QUALITY OF FERMENTED SOYBEAN BEVERAGE BY ADDITIONS OF PROPYLENE GLYCOL ALGINATE AND CALCIUM LACTATE

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ABSTRACT

A fermented soybean beverage having a low viscosity, 3.75 c.p. (crude protein, 1.54%, w/v; acidity, 0.57%, w/v as lactic acid) was prepared through a lactic acid fermentation of soymilk with Lactobacillus casei.

During the fermentation process, an organoleptically undesirable powdery-gritty sensation was developed. This off-taste could be effectively reduced by an addition of propylene glycol alginate (PGA). However, the emulsion stability of the fermented product was sometimes decreased when PGA was added. This defect could be recovered by means of an addition of some mineral salts such as calcium lactate with PGA.

As a result, a fermented soybean beverage with a smoother mouth feel and of organoleptically high value was obtained.

INTRODUCTION

In order to improve the organoleptic acceptability of soymilks, several experimental attempts to produce sour beverages or yoghurt-like products through fermentations with lactic acid bacteria have been so far carried out (Angeles and Marth 1971; Wang *et al.* 1974; Mital *et al.* 1974, 1977; Mital and Steinkraus 1975, 1976, 1979; Kanda *et al.* 1976).

However, mainly due to the difference between the characteristics

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of soybean globulins and those of milk casein, the qualities of the fermented soymilks are different from those of the traditional fermented dairy products. The most important is the development of an organoleptically undesirable powdery-gritty sensation.

Nishio *et al.* (1978) previously pointed out that the principle of this off-taste originated in some protein granules of a specific size formed when the pH of soymilk passed slowly around the isoelectric points of soybean globulins (pH 4.2 - 4.5) in the lactic acid fermentation process.

During the course of investigations on the influence of several high molecular weight additives which supposedly have electrical interactions with protein granules, it was found that the powdery-gritty sensation could be improved greatly by simply adding propylene glycol alginate (PGA) to the fermented beverage just after the usual fermentation process.

PGA has been widely used in the manufacturer of fermented dairy products such as yoghurts or acidophilus milk type products as an emulsion-stabilizer (e.g. Kambe 1974). Fermented soybean beverages even without stabilizers show much better emulsion stability over several days time than dairy products. However, the addition of PGA to fermented soymilks causes a decrease in emulsion stability. This fact indicates the great difference in the action of PGA on the fermented product from soymilk and on that from cow's milk. In this case, however, the emulsion stability of the fermented product tended to decrease depending on the amount of PGA added. This fact meant that the fermented product might undergo serum separation during storage. It was hypothesized that this defect could be prevented by the simultaneous addition of a salt of an alkaline earth metal along with the PGA. From the view point of safety as food, calcium salts such as calcium lactate seemed to be the most suitable. The emulsion stabilizing effect shown by these mineral salts was accidentally discovered in the course of experiments on fortification with minerals for nutritional purposes.

The purpose of this paper is to demonstrate by means of combination of PGA and calcium lactate, one can accomplish both the taste improvement and the high emulsion stability at the same time.

MATERIALS AND METHODS

Fermented Soymilk

The procedures for the preparation of the fermented soybean beverage used in this work, are shown in Fig. 1. A commercial product of powdered soymilk from full-fat soybeans, "Proton M" (Japan Protein Industry Co., Ltd., Tokyo) was purchased from the manufacturer and

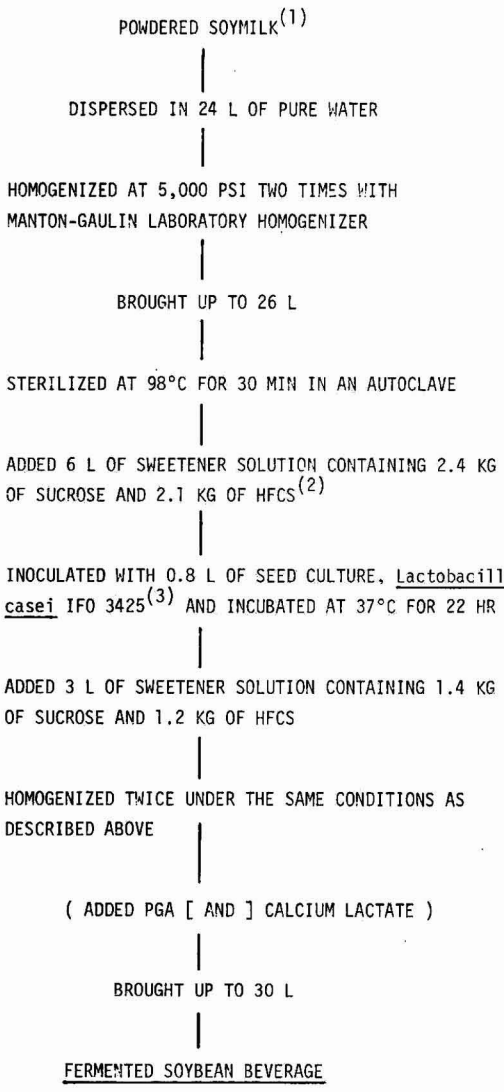

FIG. 1 PROCEDURES FOR PREPARATION OF FERMENTED SOYBEAN BEVERAGE

(1) Proton M (Japan Protein Industry Co., Ltd., Tokyo). (2) High fructose corn syrup (San Fruct; Sanmatsu Industries Co., Ltd., Tokyo). (3) A soymilk composed of 6%, w/v Proton M and 2%, w/v of dextrose, was inoculated with lactic acid bacteria and incubated at 30°C for 16 h.

employed as a starting material for the fermented product. The fermented beverage sweetened with sucrose and a high fructose corn syrup, "San Fruct" (Sanmatsu Industries Co., Ltd., Tokyo) had 1.54%, w/v of crude protein (Kjeldahl N X 6.25); 0.57%, w/v of acidity (as lactic acid) and a very low apparent viscosity, 3.75 c.p.

Propylene Glycol Alginate (PGA)

Six types of commercially available PGA preparations with low-medium viscosities, "Duckloid PF and LF", "Duckmen Ester" (Kamogawa Kasei Kogyo Co., Ltd., Tokyo), and "Kimiloid Hi-S, NLS-K and LV" (Kimitsu Kagaku Kogyo Co., Ltd., Tokyo) were purchased from the manufacturers. Among these products, Duckloid PF was used throughout the work unless otherwise stated. These PGA products were preliminarily dispersed and dissolved into pure water to make 0.5 - 4.0%, w/v solutions, and the calculated amounts of the solutions were added with a vigorous agitation to the fermented soy milk.

Apparent Viscosity

The apparent viscosity of the fermented beverage was measured at 20°C with a B-type rotary viscometer (model BL; Tokyo Keiki Co., Ltd., Tokyo).

Emulsion Stability

Ten mililiter aliquots of the fermented beverage were centrifuged for 5 min at 2000 G. The optical absorbancies at 660 nm after (a) and before (b) the centrifugation were determined. The emulsion stability was expressed in terms of a/b X 100 (%). In this definition, perfect stability was expressed as 100% (a = b).

Sensory Evaluation

The intensity of the powdery-gritty sensation developed in the fermented beverage was evaluated by the panel composed of 12 male and 8 female judges 19 - 37 years old. All of them were selected from the working staff of the laboratories for their high ability to distinguish the fermented soybean beverages with 0.05%, w/v PGA from the control in repeated triangle tests. The evaluation was carried out using a five point category scale for the intensity of powdery-gritty sensation. In this method, the intensity of the sensation of the no PGA control was defined as point 5 while, point 1 was given to the sample which showed no powdery-gritty sensation.

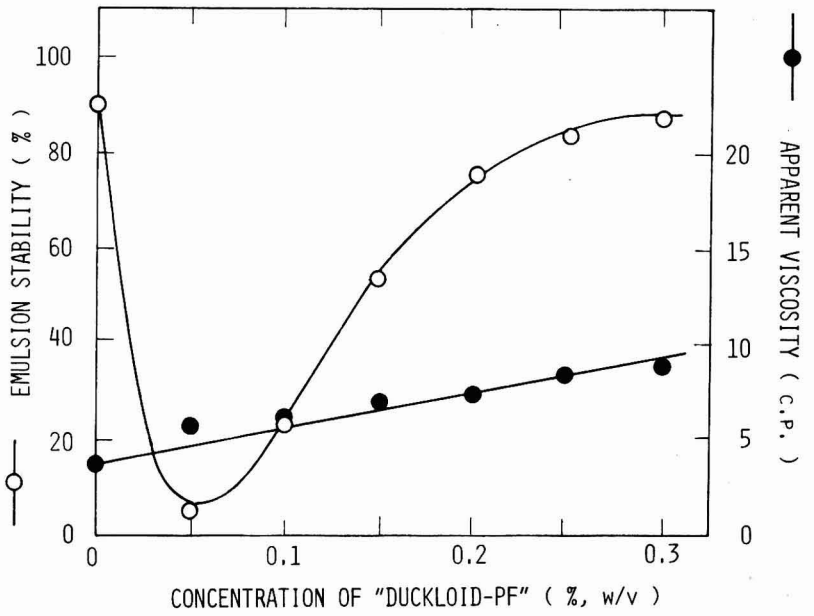

FIG. 2. RELATIONSHIP AMONG EMULSION STABILITY, APPARENT VISCOSITY AND FINAL CONCENTRATION OF PGA* IN FERMENTED SOYBEAN BEVERAGE

*Duckloid PF

RESULTS

Effect of PGA on Reduction of Powdery-Gritty Sensation of Fermented Soybean Beverage

Various concentrations of PGA solutions were added into the fermented soybean beverage, prior to standardizing the final product by an addition of water, Fig. 1. The emulsion stabilities and the apparent viscosities of the samples thus obtained were determined. Fig. 2 shows the relationship between these data and the final concentrations of PGA in the case when Duckloid PF was employed. As shown in Fig. 2, the apparent viscosity of the fermented soymilk increased gradually in proportion to the amount of PGA added, at least until 0.3%, w/v concentration.

On the other hand, the emulsion stability at first decreased markedly as the concentration of PGA increased, and showed its minimum value at 0.05%, w/v of PGA. The emulsion stability increased again above

0.1%, w/v of PGA. It showed approximately the same stability as that of the control at 0.3%, w/v of PGA. At 0.3%, w/v concentration, however, an appearance of another off flavor occured from the addition of too much PGA, concomitantly with too high a viscosity. This caused a loss in the acceptability of the beverage. On the other hand, as shown in Table 1, the taste improving effect of PGA was well recognized at the concentration higher than 0.1%, w/v. Since it seemed that a total sensory score lower than 40 was needed for the panel to conclude that the PGA was very effective at reducing the off-taste, the optimal concentration of PGA for reducing the powdery-gritty sensation was between 0.1 and 0.2%, w/v, when Duckloid PF was used as PGA.

Table 1. Organoleptic evaluation of affect of PGA[1] in reducing the powdery-gritty sensation developed in fermented soy milk

PGA (%, w/v)	Score 1	2	3	4	5	Total Score[3]
—	0[2]	0	0	1	19	99
0.05	0	8	10	2	0	54
0.10	7	7	6	0	0	39
0.15	7	8	5	0	0	38
0.20	8	8	4	0	0	36

[1] Propylene glycol alginate (Duckloid PF)
[2] Numerals show the number of subjects assigning that score.
[3] Total score is calculated by summing up the products between the scores and the number of subjects assigning that score

Influences of Type of PGA Product on Taste-Improving Effect

The effectiveness of PGA on reducing the off-taste, was not equal among the commercial PGA products tested. Some PGA products were less effective than others. Duckloid PF, Duckmen Ester and Kimiloid NLS-K showed a sensory score of 36 - 39 at 0.2%, w/v level, while Duckloid LF, Kimiloid Hi-S or LV gave a score of 42 - 48 at the same concentration.

Influences of Heat-Treatment on PGA or Fermented Beverage Added with PGA

When an aqueous solution of PGA was heat-treated, its apparent viscosity markedly decreased. In addition there were simultaneous decreases in both the taste-improving effect of PGA and the emulsion stability of the fermented beverage augmented when heat-treated. Therefore, if the PGA solution or the fermented product containing

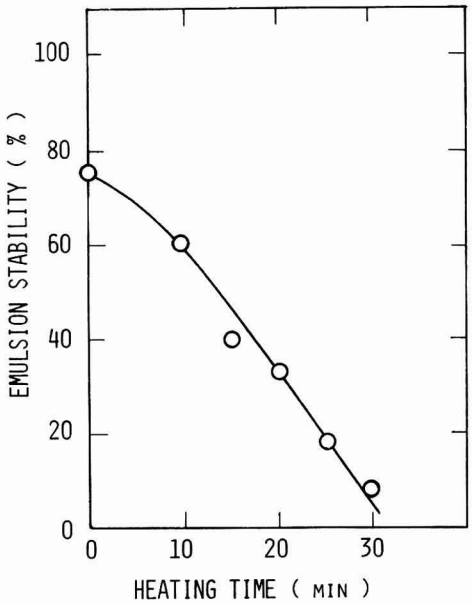

FIG. 3. EFFECT OF HEAT-TREATMENT OF PGA SOLUTION* ON EMULSION STABILITY OF FERMENTED SOYBEAN BEVERAGE ADDED WITH 0.2%, w/v OF PGA

*2%, w/v concentration of Duckloid PF

PGA needs to be heat-sterilized, it is necessary to adopt sufficiently mild conditions as to avoid these phenomena. The cause of these phenomena was assumed to be depolymerization of PGA molecules. Since an increase of the optical density at 235 nm was observed during the heat-treatment of PGA solution, a part of the depolymerization, at least, may have been through β-elimination.

The relationship between the heating time for 2%, w/v Duckloid PF solution at 95°C and the emulsion stability of the fermented beverage added with the heat-treated PGA to make 0.2%, w/v final concentration, is shown in Fig. 3.

Fortunately, the viable lactic acid bacteria in the fermented product can be completely destroyed by heat-treating at 80°C for 15 s with a plate-heater. Under these conditions, the organoleptic quality of the heat-treated product with PGA was practically the same as that of the unheated beverage.

Improvement of Emulsion Stability by Calcium Lactate

As shown in Fig. 2, a decrease of the emulsion stability of the fer-

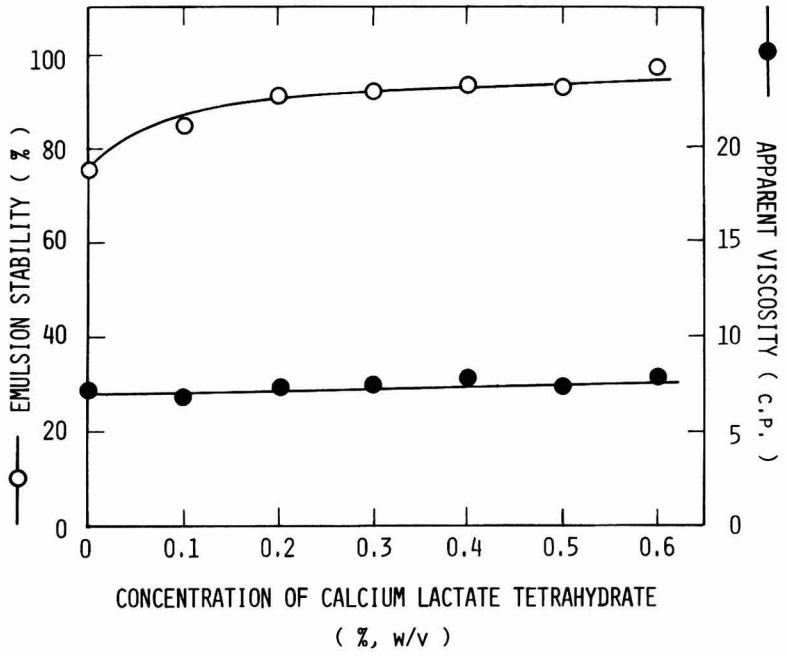

FIG. 4. EFFECT OF CALCIUM LACTATE ON EMULSION STABILITY OF FERMENTED SOYBEAN BEVERAGE CONTAINING 0.2%, w/v OF PGA*

*Duckloid PF

mented beverage was observed when PGA was added at a specific concentration range. This fact meant that serum separation might occur during storage of the fermented product. In preliminary investigations, it was demonstrated that the simultaneous addition of a water soluble salt of alkaline earth metals at 10 mM concentration with PGA, was effective in preventing the decrease of emulsion stability induced by PGA. Since calcium lactate showed almost the same effect as that of calcium chloride at the same ionic strength, the type of anion did not seem to account for the effect of mineral salts.

From the view point of safety as a food additive and also from the nutritional view point, calcium lactate was finally selected and used in the subsequent experiments. Calcium lactate was added into the fermented beverage as in the form of a 6%, w/v aqueous solution in the same way as the addition of PGA. Figure 4 shows the influence of calcium lactate concentration on the emulsion stability of the fermented beverage containing 0.2%, w/v Duckloid PF. Figure 5 shows the change of the emulsion stability of the fermented beverage during storage at

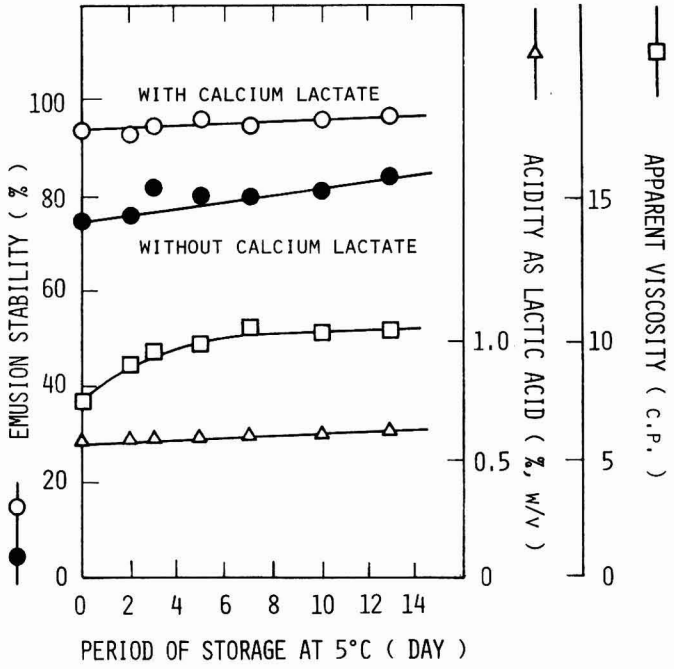

FIG. 5. CHANGE OF EMULSION STABILITY OF FERMENTED SOYBEAN BEVERAGE CONTAINING 0.2%, w/v OF PGA* DURING STORAGE WITH OR WITHOUT ADDITION OF CALCIUM LACTATE**

*Duckloid PF: **0.4%, w/v as pentahydrate

5°C with the addition of both 0.2%, w/v of PGA and 0.4%, w/v of calcium lactate pentahydrate. Slight increases in acidity and also in apparent viscosity were observed during storage. The addition of calcium lactate did not eliminate the taste-improving effect of PGA.

Influence of Protein Concentration on Organoleptic Quality of Fermented Soybean Beverage

The fermented soybean beverage prepared according to the procedures shown in Fig. 1, indicated only 1.54%, w/v of the crude protein content (Kjeldahl N X 6.25), which was almost half the concentration in cow's milk. At a higher protein concentration, the viscosity of the fermented product increased so much as to make the beverage organoleptically unacceptable. In order to avoid this defect and to produce a fermented soybean beverage of much higher protein concentration, it was possible to prepare it from an isolated soybean protein and a vegetable oil product such as a partially hydrogenated palm oil as raw

materials. A fabricated and fermented beverage thus obtained showed almost the same apparent viscosity even at 2.64%, w/v of crude protein concentration. The same effects of PGA and calcium lactate were also seen in this fabricated product.

DISCUSSION

As described before, the taste-improving effect of PGA was attributed to its electric interaction with protein granules which were assumed to be the principle of powdery-gritty sensation. Since some PGA preparations are less effective than others, the change in their structures, such as the specific ester distribution may be the factor accounting for the taste improving effect. However, according to the preliminary experiments on the PGA products tested in this work, the differences in the degree of esterification, the degree of polymerization or the intrinsic viscosity $[\eta]$ did not seem to account for sensory differences among the products. More detailed investigations, including structure analyses of the PGA products, will be needed in future. The emulsion-stabilizing effect of calcium lactate may also attribute to the interaction with protein granules. Calcium ions show an interaction with PGA as indicated by the control of viscosity.

At the present time, however, no data can be shown to support the speculations described above.

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INFLUENCE OF MATURITY, STORAGE AND HEATING ON THE FLAVOR OF MUSHROOM (*AGARICUS BISPORUS*) CAPS AND STEMS

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ABSTRACT

Sensory data indicated that raw caps (Agaricus bisporus) had a higher degree of desirable mushroom aroma than raw stems, however, cooked caps and stems were judged to be the same in aroma. Medium sized mushrooms were generally found to have more desirable aroma than small or large mushrooms. Storage for up to 7 days was detrimental to raw and cooked cap and stem aromas.

Gas chromatographic analysis revealed that the level of 1-octen-3-ol and 1-octen-3-one increased with maturity, storage and cooking with higher levels of both found in the caps as compared to the stems. Correlation of sensory and analytical data indicate that 1-octen-3-ol is associated with desirable mushroom aroma whereas 1-octen-3-one is not. Information of this type should be useful in the harvesting and distribution of mushrooms.

INTRODUCTION

Although the mushroom has pleasant and characteristic organoleptic properties, few published studies exist on its sensory and volatile composition.

A sensory study by Bernhard and Simone (1959) in which the common field mushroom *Agaricus campestris* was utilized demonstrated that various portions of this mushroom can have significantly different aroma intensities. For example, the gills were found to have less aroma than the intact cap versus the intact stem. Another group (Abbott and San Antonio 1974) compared the overall sensory properties of the cultivated mushrooms *Agaricus bisporus* and *Agaricus bitorquis.* They found that 38% of their panel preferred the former, 24% the latter, and 38% had no preference.

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Research on the flavor chemistry of mushrooms would indicate that both volatile (Cronin and Ward 1971; Thomas 1973; Picardi and Issenberg 1973; Wasowicz 1974; Pyysalo 1976; Pyysalo and Suihko 1976; Card and Avisse 1977) and nonvolatile components (Craske and Reutter 1965; Dijkstra and Wiken 1976a,b) are important. However, the work of Pyysalo and co-workers convincingly demonstrated that volatiles such as 1-octen-3-ol and 1-octen-3-one, because of their sensory properties and odor thresholds, play a major role in fresh and cooked mushroom aroma.

The influence of cooking on resulting mushroom aroma has been briefly investigated by two groups. Picardi and Issenberg (1973) reported that 1-octen-3-one appeared after boiling *Agaricus bisporus* for 15 min. Card and Avisse (1977) also compared the volatiles associated with raw and cooked *Agaricus bisporus* and although it was not apparent from their data, they reported increases in carbonyls upon cooking.

As with all raw agricultural commodities, harvesting does not terminate metabolic activity, and thus, many changes can occur during storage. In the case of mushrooms, Hammond (1978) reported that significant enzymatic activity relative to carbohydrate catabolism occurred after harvest. This in turn could result in flavor changes, especially upon heating.

In light of the above, several objectives were defined for the current study. These included: (1) To determine by sensory and instrumental means any possible odor differences in raw and heated *Agaricus bisporus* attributable to stage of maturity, storage conditions and location in the mushroom (cap versus stem). (2) To measure relative and semiquantitative changes in 1-octen-3-ol and 1-octen-3-one as influenced by the variables described above. (3) To attempt to relate differences in 1-octen-3-ol and 1-octen-3-one concentrations with sensory panel data.

MATERIALS AND METHODS

Stages of Maturity

Commercially available *Agaricus bisporus* were utilized which were harvested at three different stages of maturity. The first stage was a button stage where the caps were 10-15 mm in diameter and the stems 15-20 mm in length. The medium stage was represented by caps 20-25 mm in diameter with closed veils and stems 30-35 mm long. The large stage had open veils with caps 30-40 mm in diameter and the stems 40-50 mm long.

Storage Conditions

Immediately after harvest any visable dirt was lightly brushed off and the stems were cut from the caps and stored separately in sealed plastic containers under three conditions. The first served as the control and represented sensory and chemical evaluation within three hours of harvest. The second condition was designated commercially fresh and represented products that were held for 48 h at 10°C. The last group was held for 168 h (7 days) at 10°C.

Sample Preparation

Just before sensory evaluation caps and stems were removed from storage and cut into 3-4 mm pieces to minimize visual differences. Approximately 25 g portions of raw or cooked product were placed into clean and odor free 100 ml glass beakers that were covered with aluminum foil to minimize visual differences. These were each immediately covered with a watchglass and they were served to the panel. Cooking was accomplished in a nonstick surface frying pan with a tight fitting lid whereby 500-g units of product with no additives were heated on an electric stove with agitation for 5 min on medium high heat. The frying pan was removed from the heat and the cooked product was permitted to cool covered for 5 min before 10 g samples were removed for sensory evaluation.

Sensory Evaluation

A 20 member college-age panel consisting of 12 females and 8 males who were enrolled in a sensory evaluation class was asked to score the degree of desirable mushroom aroma on a 1-10 scale with 1 being most desirable. The samples were not tasted. One sample was served at a time with six samples being served at a session. Each session represented the ramdomly presented stems and caps of the three different maturity stages from the storage condition. Each maturity/storage condition was ramdomly repeated three times. Sampling was conducted in mid-afternoon on 9 consecutive weekdays. The sampling was repeated twice and therefore, each variable was presented for a total of 60 evaluations. Thus, a total of 2160 observations were performed. Composite means were calculated and statistically evaluated.

Isolation of Volatiles

Volatiles were isolated essentially as by Pyysalo (1976) whereby three 1000-g replicates of raw or cooked mushroom representing each variable were pressed to yield juice samples which were steam distilled

under sufficient vacuum so that the temperature did not exceed 35°C. The resulting condensate was continuously extracted for 24 h into an ether-pentane (1:1) mixture. This extract was then concentrated to approximately 50 μL under vacuum. The concentrates from each of the three batches were combined to form a composite sample for gas chromatographic analysis.

Separation and Identification of Volatiles

A Hewlett Packard Model 5830A gas chromatograph equipped with a flame ionization detector and a Model 18850A terminal programmed to calculate relative percent peak areas were utilized. Column type and operational conditions were the same as reported by Dijkstra and Wiken (1976b). For the purpose of the current study, only the relative levels of the compounds 1-octen-3-ol and 1-octen-3-one were determined since from the literature discussed above, these compounds are apparently the primary organoleptically significant volatiles associated with mushroom aroma. The separation of these compounds under the conditions employed made identification based on the retention times of authenitic compounds a relatively easy task.

Based on uniform sample size and injection technique, an attempt was made to semi-quantitate the two compounds in question relative to observed peak area responses for known amounts of injected compounds.

RESULTS AND DISCUSSION

Sensory Evaluation

In contrast to the work of Bernhard and Simone (1959), who found no significant difference in aroma intensity between cap and stem in the raw and steamed state, a significant difference in aroma desirability was found between raw caps and stems independent of maturity and storage time with, in all cases, the caps having the more desirable aroma (Table 1). Quite possibly, the evaluation of different mushroom varieties in the two studies can account for this difference, since the sensory properties among varieties can vary dramatically (Pyysalo 1976). The current study utilized the primary commercial variety available in the United States.

The specific effects of maturity and storage indicated that desirable raw cap aroma was primarily associated with the medium and large sized, fresh products. However, in the case of raw stems, the fresh,

Table 1. Sensory data summary

Maturity	Storage Time	Caps		Stems	
		Raw	Cooked	Raw	Cooked
Button	Fresh	4.3 b,B	3.2 b,A	5.1 b,C	3.0 b,A
	2 days	4.4 b,B	3.4 b,A	5.4 c,C	3.1 b,A
	7 days	5.5 c,B	4.4 c,A	6.2 d,C	4.6 d,A
Medium	Fresh	3.5 a,B	2.3 a,A	4.8 b,C	2.5 a,A
	2 days	3.7 a,B	2.5 a,A	4.9 b,C	2.5 a,A
	7 days	4.6 b,B	3.4 b,A	5.6 c,C	3.7 c,A
Large	Fresh	3.7 a,B	3.0 b,A	4.3 a,C	3.2 b,A
	2 days	4.4 b,B	3.3 b,A	5.5 c,C	3.3 b,A
	7 days	5.9 c,B	5.1 d,A	7.3 e,C	4.9 d,A

Data with different small letters, within each column, are significantly different from each other (α=0.05).
Data with different large letters, within each row, are significantly different from each other (α=0.05).
The lower the number, the more desirable the mushroom aroma

large product was most desirable. As perhaps would be expected, storage of raw caps and stems for 7 days resulted in the most inferior products. The same general trends were observed for both cooked caps and stems. Interestingly, button mushrooms overall did not score significantly better in desirable aroma than the other two stages of maturity independent of other variables evaluated. It would also appear that utilization of raw stems that have been stored for a length of time could influence consumer acceptance of such a product, since they scored poorer than the corresponding raw caps. However, it should be noted that cooking improved both the stems and the caps, but it exerted a greater improvement on the stems, since cooked stems were essentially the same as cooked caps even though the aroma of raw stems was poorer than that of raw caps.

Volatile Evaluation

Based on sensory characterization (Cronin and Ward 1971; Pyysalo and Suihko 1976), threshold (Pyysalo and Suihko 1976), and formation data (Picardi and Issenberg 1973) for 1-octen-3-ol and 1-octen-3-one, several interesting trends are noted in the semi-quantitation of these compounds in the current study. This information is summarized in Table 2.

The amount of these two compounds was shown to increase with maturity and storage time, thus indicating the role of metabolic activity

Table 2. Total PPM and ratio (1-octen-3-ol/1-octen-3-one) of volatiles as influenced by cooking, maturity, location and storage time

		Caps				Stems			
		Raw		Cooked		Raw		Cooked	
Maturity	Storage Time	Level	Ratio	Level	Ratio	Level	Ratio	Level	Ratio
Button	Fresh	6.2	—[1]	6.5	—	5.5	—	5.7	—
	2 days	6.5	—	6.6	—	5.8	—	6.1	—
	7 days	7.1	—	7.5	1700	6.3	—	6.5	—
Medium	Fresh	8.0	1200	8.5	810	7.7	1560	8.2	1050
	2 days	8.4	1130	8.8	450	7.7	1290	8.4	930
	7 days	9.3	940	9.7	260	8.4	1080	8.9	430
Large	Fresh	8.9	740	9.5	310	8.1	910	9.5	720
	2 days	9.0	680	9.7	180	8.5	760	9.6	630
	7 days	9.7	310	10.5	20	9.2	580	9.9	250

[1] Variables with no reported data due to lack of detection of 1-octen-3-one

(Hammond 1978) in the formation of these compounds. Higher levels of both were found in the caps than the stems independent of other variables, thus explaining the sensory differences noted, especially in the raw state.

Cooking was also found to increase their levels, thus pointing out the potential for their thermal formation. This is especially true for 1-octen -3-one and thus supports the observation of Picardi and Issenberg (1973).

Thus, these analytical data support the sensory observations since apparently at high concentrations 1-octen-3-ol and 1-octen-3-one can lead to too intense or objectionable aromas, thus decreasing the overall aroma acceptability of mushrooms. The data also indicate that based on the levels produced during storage, 1-octen-3-ol is associated with desirable mushroom aroma whereas 1-octen-3-one is more closely associated with undesirable aroma. In addition, the variables increased the concentration of 1-octen-3-one by a factor of approximately 100 whereas they influenced 1-octen-3-ol concentration by a factor of only two. Thus, it would appear that the formation of the latter compound is more active than the former.

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PRODUCTION OF SOY ISOLATES BY ULTRAFILTRATION: PROCESS ENGINEERING CHARACTERISTICS OF THE HOLLOW FIBER SYSTEM

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ABSTRACT

The effect of various performance parameters on flux during the hollow fiber ultrafiltration of defatted soy flour extracts was studied. Flux was significantly affected by pressure up to the limits of the unit. Higher temperatures also increased flux. However, flow rate had practically no effect. Also, no hysteresis effects were observed upon lowering the pressure from the highest to lowest values. The data indicated that concentration polarization or mass transfer was not rate-controlling and flux behavior could be modelled by momentum transfer considerations. A modified power law version of the Poiseuille equation, $J = A\ (\Delta P_T)^n$, best fit the data, where J is the flux, ΔP_T is the transmembrane pressure and A and n are constants characteristic of a particular membrane-feed combination. A and n decreased with increasing solids in the feed, and A increased while n decreased with increasing temperature.

INTRODUCTION

In an ultrafiltration (UF) process, permeate flux and solute rejection are the most important performance characteristics. Since UF is basically a hydraulic pressure-activated process, parameters expected to have the greatest influence on permeate flux are those that affect the fluid dynamics of the system such as temperature, transmembrane pressure, feed composition and flow rate or velocity past the membrane surface. Due to its relatively high selectivity and mild operating conditions, UF has proven to be extremely useful in fractionating, purifying and concentrating macromolecules in solution, with the greatest applications to date in the dairy industry. We have recently developed processes

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for the production of highly functional protein concentrates from water extracts of whole soybeans (Omosaiye and Cheryan 1979) and isolates from defatted soy flour (Nichols and Cheryan 1981). In this paper, we report on the process engineering and performance characteristics of the hollow fiber-defatted soy flour water extract system with a view towards understanding the phenomenon and optimizing the factors that control permeate flux.

MATERIALS AND METHODS

Water Extracts of Defatted Soy Flour

The feed was prepared by multiple extraction and centrifugation. One part by weight defatted soy flour (Nutrisoy 7B, Archer Daniels Midland Company, Decatur, IL) was suspended in 9 parts by weight tap water at pH 9, 30°C for 30 min. The slurry was centrifuged in a Westfalia Laboratory Separator-cum-Desludger (Model SAOH 205). The residue from the first extraction was resuspended in 10 parts by weight tap water and centrifuged again. The number of extractions and/or flour-to-water ratio was adjusted to give the required solids concentration in the feed. The relevant physical properties of the feed, viscosity (μ) and density (ρ), were obtained as described earlier (Cheryan 1977) and are shown in Fig. 1 and 2. Total solids (T.S.) and protein content (N x 6.25) were determined using standard methods (Nichols and Cheryan 1981). Table 1 shows the proximate composition of the various feeds.

Ultrafiltration

A pilot scale hollow fiber unit was used in all experiments (HF1SS, Romicon, Inc., Woburn, MA). Two membranes were evaluated: PM30 (43) and XM50 (45). Both were in the form of 660 noncellulosic hollow fibers of 63.5 cm length, with a total surface area of 1.39 m^2 each. The PM30(43) module fibers, reportedly made of polysulfone, had an internal diameter of 0.109 cm and a nominal molecular weight cut-off of 30,000. This module had not been used prior to these experiments. The XM50(45) module fibers, reportedly an acrylic vinyl copolymer, had an internal diameter of 0.114 cm and a 50,000 molecular weight cut-off. This module had been purchased ten months earlier and had about 20 h of use prior to these experiments.

Valves and pressure gauges at the inlet and outlet of the cartridge enabled transmembrane pressure to be varied independent of flow rate

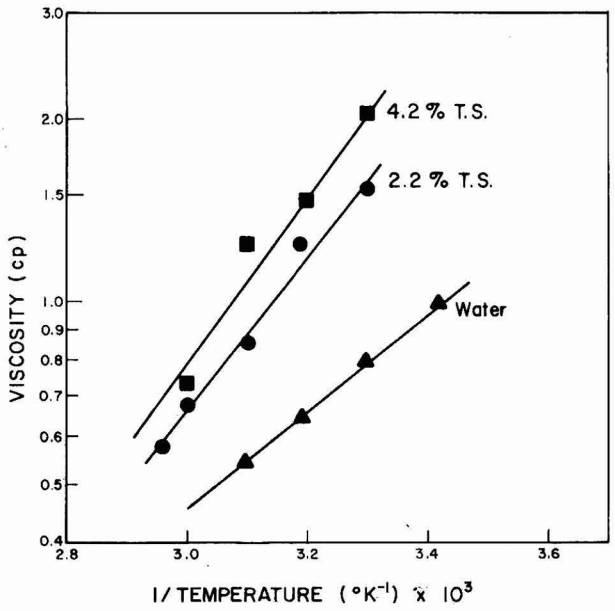

FIG. 1. EFFECT OF TEMPERATURE ON VISCOSITY OF DEFATTED SOY FLOUR EXTRACTS

Table 1. Proximate composition of feed solution (% w/w)

Feed Solution	Total Solids	Protein	Ash	Carbohydrate[a]	Fat[b]
A	2.6	1.6	0.21	0.79	—
B	4.0	2.7	0.29	1.01	—
C	4.2	2.7	0.29	1.21	—

[a]By difference
[b]Negligible. Less than 0.05%

within certain limits. Transmembrane pressure is expressed as the average of the inlet (P_i) and outlet (P_o) pressures. Flow rate of feed/retentate is expressed in terms of pressure drop (P_i-P_o) which is related to flow rate as shown in Fig. 3. Flow rate was measured using a Signet MK366 Magnetic Flosensor System (Signet Scientific Company, El Monte, CA) mounted in the retentate return line. Permeate flux was measured using a Gilmont flow meter Model 3205 (Cole Parmer, Chicago, IL). Temperature was maintained to ± 1°C by adjusting the steam or cold water flow rates to the jacketed feed tank.

In the ultrafiltration of macromolecular solutions, the effects of

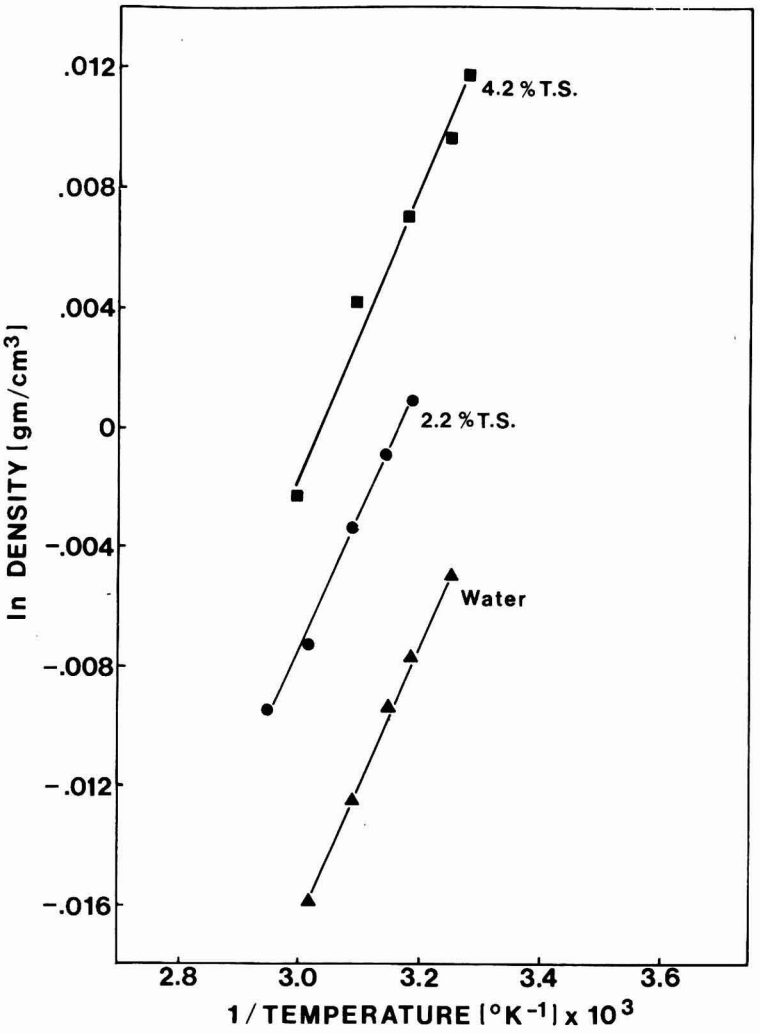

FIG. 2. EFFECT OF TEMPERATURE ON DENSITY OF DEFATTED SOY FLOUR EXTRACTS

operating parameters such as transmembrane pressure, temperature and flow rate on permeate flux are evaluated at constant feed composition. This was achieved in our study by continuous recycle of both retentate and permeate to the feed tank. Permeate flux readings were taken when the system reached a pseudo steady state (Cheryan 1977), i.e., when permeate flux stabilized, generally within 5 min of setting the three parameters.

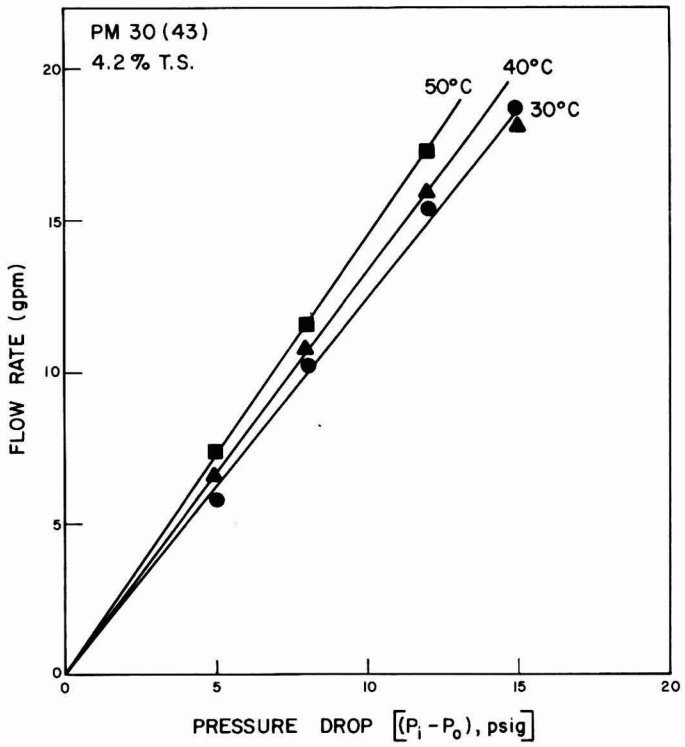

FIG. 3. RELATIONSHIP BETWEEN PRESSURE DROP AND FEED FLOW RATE FOR PM30 (43) HOLLOW FIBER CARTRIDGE

RESULTS AND DISCUSSION

Theory: Models for Predicting Flux

A number of theoretical models based on various mechanisms of membrane transport are described in the literature. It is generally believed that the best description of macroporous membranes is given in terms of the Hagen-Poiseuille law for flow through channels:

$$J = \frac{\epsilon R^2 g_c \Delta P_T}{8 \mu \Delta x} \quad (1)$$

where

J = water flux, volume per unit membrane area per unit time
R = radius of pore

μ = viscosity
Δx = membrane thickness
g_c = gravitational constant
ϵ = number of pores per unit membrane area
ΔP_T = transmembrane applied pressure

For real UF membranes, variations in pore size distribution, shape and tortuosity will affect the relationship given in eq. 1. A correction, known as the tortuosity factor, is usually included in the above expression to account for the deviation. The tortuosity factor for a specific polysulfone membrane was recently estimated from electron micrographs to vary from 0.04 to 0.08 (Merin and Cheryan 1980a).

For a particular membrane-feed combination, Eq. 1 is usually written as:

$$J = A \Delta P_T \tag{2}$$

where A is the Membrane Permeability Coefficient, analogous to U, the overall heat transfer coefficient in the heat transfer equation Q=U. A. ΔT. The permeability coefficient can also be written in terms of a series of resistances to solvent flow as:

$$A = 1/(R_m + R_g + R_f) \tag{3}$$

where R_m is the resistance to solvent flow due to the membrane itself, R_g is the resistance due to the concentration polarization or macromolecular "gel" layer built up at the membrane surface by convective transport, and R_f is the additional resistance due to any fouling of the membrane. R_m is a function of membrane properties and membrane-solvent interactions and is best determined in terms of the flux behavior of water. R_g and R_f are functions of the physical properties of the feed and operating conditions. R_f is also affected by specific membrane-solute interactions. The relative importance of R_f in determining overall membrane permeability increases with operating time or cumulative volume permeated (Merin and Cheryan 1980b), depending on the extent of fouling of the membrane. For this study, R_f is assumed to be negligible since the optimization is based on initial flux data. In addition, separate studies have shown there is negligible membrane-solute interaction at the low feed concentrations considered here (Nichols and Cheryan 1981).

Experimental Results

In an earlier study (Cheryan and Nichols 1980), Response Surface

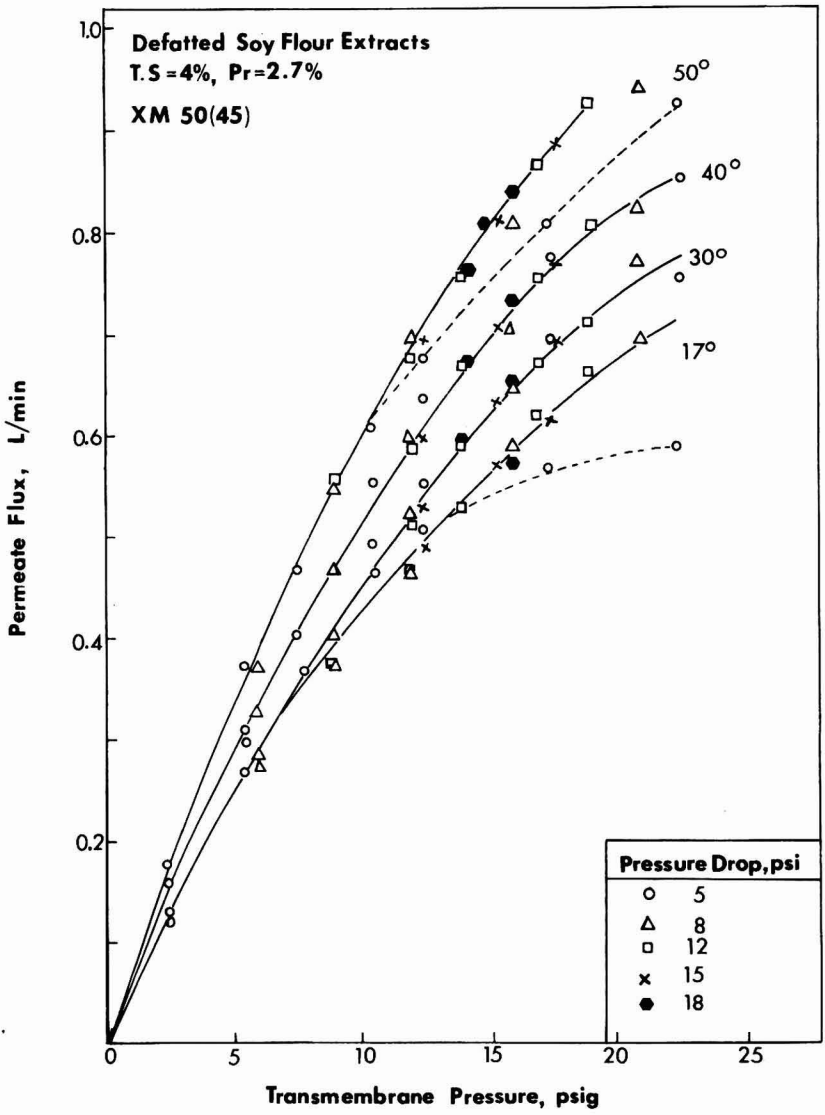

FIG. 4. EFFECT OF TRANSMEMBRANE PRESSURE, TEMPERATURE AND FLOW RATE ON PERMEATE FLUX USING THE XM50(45) MEMBRANE AND DEFATTED SOY FLOUR EXTRACTS

(Feed Solution B; see Table 1)

Methodology (RSM) was used to identify important variables governing the UF process. A two-level factorial design was used to determine the path of steepest ascent towards the neighborhood of optimum process response (flux). Then a central composite design was used to de-

velop a second order polynominal approximation of the true response (Nichols 1980). Physical constraints of the equipment limited the extent to which RSM could be applied. However, that study did identify pressure and temperature as the most important variables, while flow rate appeared to have little or no effect. The RSM study served as an informed starting point for the development of the mechanistic models which are described here. Because they are based on sound physicochemical theories, mechanistic models give a better understanding of the ultrafiltration phenomenon than the empirical models developed using statistical techniques.

Figure 4 shows typical effects of transmembrane pressure, flow rate (in terms of pressure drop) and temperature on permeate flux for low feed concentrations. Flux is significantly pressure and temperature dependent up to the limits of the unit, which in the case of the XM50 (45) cartridge was 25 psig (172 kPa) and 50°C, respectively. Flow rate through the fibers (indicated by pressure drop) has little or no effect except at the highest pressures. In addition, the flow rate effect is observed only at low flow rates. Once the flow rate is above 19-27 liters/min (pressure drop of 5 psig), it has no effect on flux. Also, little or no hysteresis was observed upon lowering the transmembrane pressure from the highest to lowest values. Almost identical affects were observed with the PM30(43) cartridge (Fig. 5). A study done with more dilute extracts (2.6% total solids) and the XM50(45) membrane showed similar trends except that there was even less curvature in the pressure-flux relationship and flow rate had no effect even at the highest pressures (not shown; Nichols 1980).

The data indicate that concentration polarization effects are not rate-controlling in this particular system (although the beginning of asymptotic flux behavior can be noticed at higher pressures in Fig. 4 and 5). This is in contrast to the full-fat soybean extract-hollow fiber system studied by Cheryan (1977) which showed classic concentration polarization effects at lower solids and protein concentrations. In that system, flux became independent of pressure at fairly low pressures and was significantly affected by temperature and flow rate. Efforts to improve permeate flux were focused on improving the mass transfer characteristics of that system. In the hollow fiber-defatted soy flour system studied here, a momentum transfer approach to modelling flux (based on Eq. 2) could be used since concentration polarization was not limiting (within the allowable pressure constraints of the unit and at low feed concentrations).

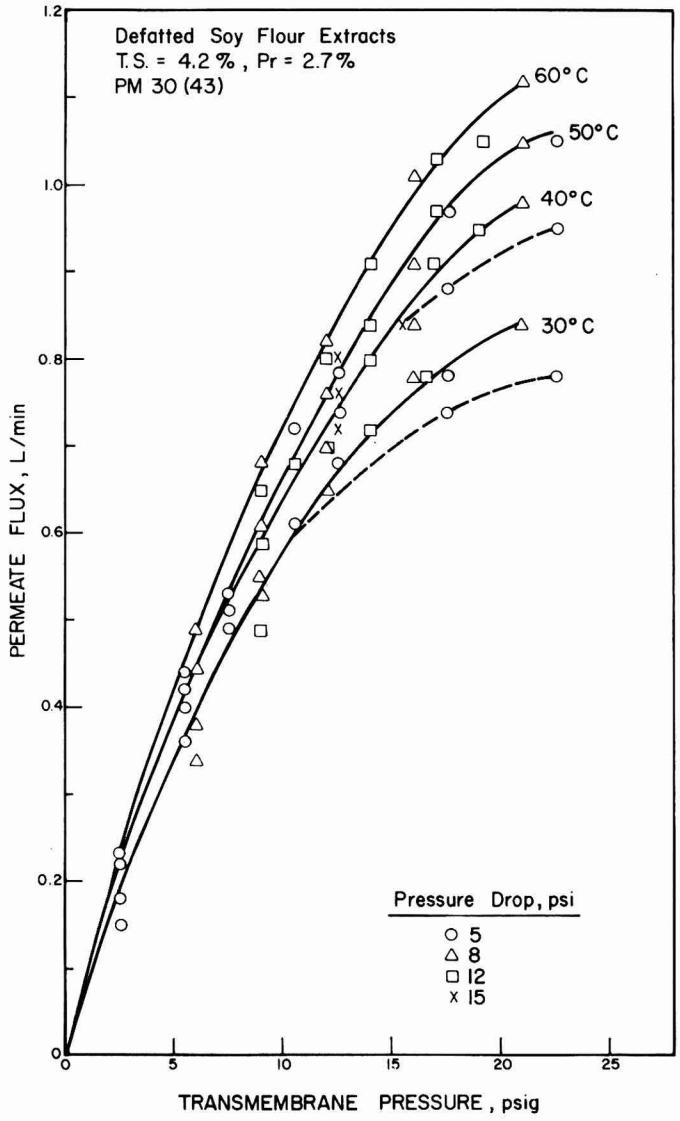

FIG. 5. EFFECT OF TRANSMEMBRANE PRESSURE, TEMPERATURE AND FLOW RATE ON PERMEATE FLUX USING THE PM30(43) MEMBRANE AND DEFATTED SOY FLOUR EXTRACTS

(Feed Solution C; see Table 1)

Membrane Permeability Coefficients

Values of A for various membrane-feed combinations were calculated and are shown in Table 2. The A values for water for either membrane were much higher than those for soy extracts, indicating that the value of R_g in Eq. 3 would be much higher than R_m. There was no significant difference between the two membranes when processing the soy extracts, suggesting that any differences in pore size distribution and other membrane properties are not large enough to affect flux, although the age and prior use difference between the modules could be a factor.

Table 2. Membrane permeability coefficients, A ($L/m^2/h/kPa$) using Eq. 2, $J = A \Delta P_T$, (for water and soy extracts)

Membrane	Feed	30°C	40°C	50°C	60°C
XM50 (45)	Water	1.20	1.25	1.28	—
	B (4.0% T.S.)	0.21	0.23	0.26	—
PM30 (43)	Water	1.03	1.08	1.10	—
	C (4.2% T.S.)	0.23	0.25	0.29	0.30

A values calculated as the slopes of the regression curves of J vs ΔP_T

Table 2 also shows that the membrane permeability coefficient increases with temperature. This is not unexpected since A as expressed in Eq. 2 includes the viscosity of the permeate (compare Eq. 2 with Eq. 1). To account for the effect of viscosity (μ) on flux, the pore flow model is usually written as:

$$J = A' \frac{\Delta P_T}{\mu} \tag{4}$$

Since viscosity decreases with temperature (Fig. 1), flux and A should increase with temperature as the data in Table 2 suggests. However, an interesting phenomenon occurs when A′ values are calculated (Table 3). If viscosity alone could account for the effect of temperature on flux, A′ values should be unaffected by temperature for pressure-controlled systems (Cheryan and Schlesser 1978; Eakin *et al.* 1978). However, A′ values now decrease with temperature (Table 3). This indicates that factors other than viscosity affect flow through membrane pores in the pressure-controlled region.

Three factors not directly accounted for in calculations so far are density, osmotic pressure and compaction effects. The density (ρ) of

Table 3. Membrane permeability coefficients, A′ (L.cp/m^2/h/kPa) using Eq. 4, $J = A' \Delta P_T/\mu$, (for water and soy extracts)

Membrane	Feed	30°C	40°C	50°C	60°C
XM50 (45)	Water	0.96	0.82	0.70	—
	B (4.0% T.S.)	0.17	0.15	0.14	—
PM30 (43)	Water	0.82	0.71	0.60	—
	C (4.2% T.S.)	0.18	0.16	0.16	0.14

A′ calculated as the slopes of linear regression curves of J vs $\Delta P_T/\mu$

water and soy extracts decrease with temperature (Fig. 2) and perhaps kinematic viscosity (μ/ρ) would be a better parameter to use in Eq. 4 than viscosity (μ). However, the relative decrease in density is less than the decrease in A′ and hence it is probably only a small contributor to the phenomenon. Osmotic pressure has generally been ignored in such calculations. The actual driving force for flux is not ΔP_T as written in Eq. 1, 2 and 4, but ($\Delta P_T - \Delta\pi$), where $\Delta\pi$ is the transmembrane osmotic pressure against which ΔP_T is applied. $\Delta\pi$ has been neglected in protein ultrafiltration because its absolute value is very small. For example, assuming protein rejection is 100% (Nichols and Cheryan 1981) and a mean molecular weight of 100,000, the Van't Hoff equation results in a $\Delta\pi$ of 0.117 psi at 50°C. This is negligible as compared to the applied pressure in most cases and, hence, $\Delta\pi$ is usually neglected. However, such logic is simplistic since it neglects the osmotic pressure exerted by the many small molecules such as the minerals and oligosaccharides present at the membrane surface as a result of interaction with the rejected protein in the concentration polarization layer. If the contribution of these components is also included, the osmotic pressure contribution may become significant, especially if the second virial coefficient in the osmotic pressure expression is also considered (Goldsmith 1971). In that case, as temperature increases, osmotic pressure also increases, which decreases the overall driving force. This possibility was suggested by Kozinski and Lightfoot (1972), but has rarely been considered in protein ultrafiltration. One particular problem in food systems is the lack of good osmotic pressure or molecular weight data.

A third factor that cannot be precisely quantified is compaction effects. Compaction of the membrane pores or of the concentration-polarization layer under pressure will increase the resistance to solvent transport, an effect that is more noticeable at higher pressures and temperatures. This, in turn, would contribute to the greater deviation from linearity at higher pressures observed in Fig. 4 and 5 and the decreasing A′ values with increasing temperature (Table 3).

Power Model for Flux-Pressure

Figures 4 and 5 show that the relationship between ΔP_T and J is not strictly linear and there is significant curvature in the data. To describe the data better, Eq. 2 can be modified to a semi-empirical power model as follows:

$$J = A_n \ (\Delta P_T)^n \tag{5}$$

In this model, "n" accounts for the curvature in the relationship and can have values between 0 and 1.0. Table 4 shows values of n and Table 5 shows values of A_n. The lower the value of n, the faster the system approaches pressure independent flux behavior and becomes mass-transfer controlled. As expected, n values decrease with increasing feed concentration (Table 4). This is due to the greater ease with which the limiting gel layer is formed at higher feed concentrations, thus increasing the relative importance of concentration polarization. Table 4 also shows that n values decrease with increasing temperature which could be related to the osmotic pressure and membrane compaction effects that were discussed earlier and are not included in the power model (except indirectly in terms of n). A_n values shown in Table 5 have the same relative trends as seen in Table 2 for A and the same interpretations are applicable here. Similarly, further modification of Eq. 5 could be made to include both curvature and viscosity effects and a similar set of A_n' values obtained (not shown).

Table 4. "n" values for the power model, Eq. 5, $J = A_n (\Delta P_T)^n$, (for water and soy extracts)

Membrane	Feed	30°C	40°C	50°C	60°C
XM50 (45)	Water[1]	1.00	1.00	1.00	—
	A (2.6% T.S.)	0.96	0.93	0.92	—
	B (4.0% T.S.)	0.78	0.77	0.76	—
PM30 (43)	Water[1]	1.00	1.00	1.00	1.00
	C (4.2% T.S.)	0.76	0.72	0.73	0.72

[1] Theoretical. In practice, some deviation was observed. "n" calculated as slopes of linear regression lines of log J vs log ΔP_T

It should also be mentioned that even though the PM30(43) membrane's maximum operating temperature recommended by the manufacturer is 75°C, we obtained a pseudo-optimum temperature of 60°C. During the RSM study mentioned earlier, we observed that although operating at 65°C or higher resulted in high initial flux (> 65 liters/m^2/h),

Table 5. Membrane permeability coefficients, A_n ($L/m^2/h/kPa$) for power law model Eq. 5, $J = A_n (\Delta P_T)^n$. (for water and soy extracts)

Membrane	Feed	30°C	40°C	50°C	60°C
XM50 (45)	Water	1.20	1.25	1.28	—
	B (4.0% T.S.)	0.71	0.84	0.99	—
PM30 (43)	Water	1.03	1.08	1.10	—
	C (4.2% T.S.)	0.92	1.19	1.26	1.36

Calculated as slopes of linear regression lines of J vs $(\Delta P_T)^n$. n values from Table 3

a rapid and continuous decline in flux occurred, regardless of applied pressure, and steady-state was not achieved within the time frame of the other experimental points (Cheryan and Nichols 1980). In addition, cleaning the membrane cartridge and restoring initial water flux was considerably more difficult. These effects were not observed at any temperature below 60°C. The high temperatures, perhaps aggravated further by the high shear rates in hollow fibers, may have denatured the proteins and/or activated membrane-protein interactions resulting in severe fouling of the membrane. For this reason, no studies were conducted above 60°C.

Effect of Feed Concentration

Permeate flux declined rapidly for both membranes as the feed concentration increased (Fig. 6). At higher concentrations, the viscosity of the feed increases and it becomes easier for the (gel) polarization layer to form on the membrane surface. Hence, the thickness of the concentration polarization (gel) layer and the effect of the hydrodynamic boundary layer next to it increase at higher concentrations. These effects combine to increase resistance to mass transfer with a concomitant reduction in the permeate flux when all other factors are constant. Optimization of flux will then have to be approached from the mass transfer viewpoint rather than from momentum transport considerations (Cheryan 1977).

It is interesting to note that when the data were extrapolated to zero flux, the intercept on the concentration axis was different for the two membranes. The XM50(45) membrane would apparently cease operation at 22% total solids (20% protein), whereas the PM30(43) could tolerate much higher feed concentrations (29% total solids and 26% protein). The fiber diameters, pore size, operating conditions and initial flux are not significantly different for the two membranes. However, the membranes are made of different polymers. This indicates the like-

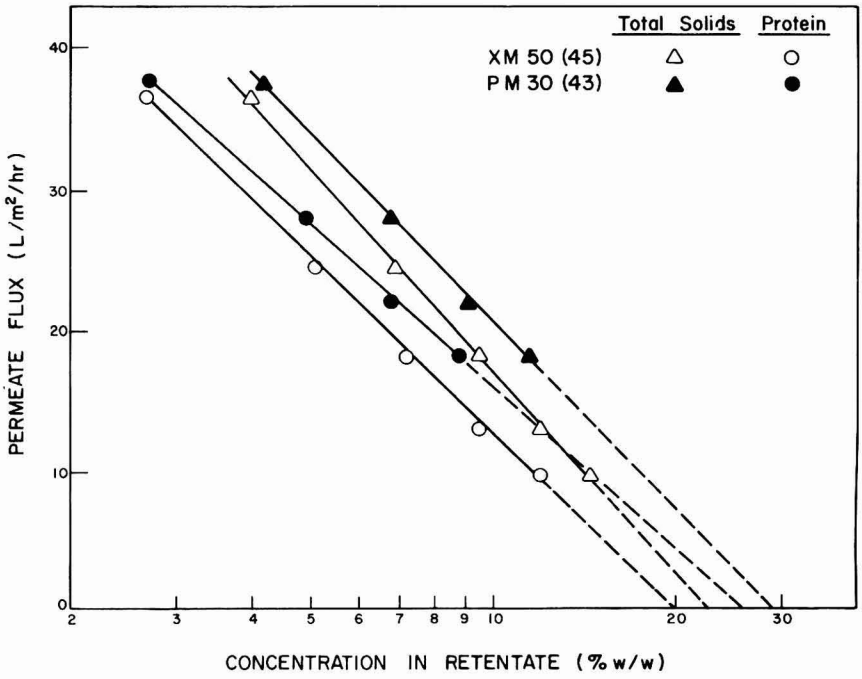

FIG. 6. EFFECT OF TOTAL SOLIDS AND PROTEIN CONCENTRATION ON PERMEATE FLUX

($P_i = 25$ psig, $P_o = 15$ psig, Temperature = 50°C).

lihood of a specific membrane-protein interaction leading to greater "fouling" effects, i.e., the PM30(43) membrane apparently "fouls" less than the XM50(45) membrane with this particular feed. This has been confirmed in a separate parallel study of the adsorption characteristics of these two membrane polymers (Nichols and Cheryan 1981).

Comparison of different UF units

It is difficult to compare data in the literature since most are not reported in terms of a universal parameter such as the membrane permeability coefficient (A). Instead, most data are reported in terms of flux, which is analogous to reporting heat transfer data in terms of Q (rate of transfer of heat) instead of the more meaningful U (overall heat transfer coefficient). Despite the relatively low pressure limits specified for hollow fiber units, their performance is comparable to many other units. For example, Lawhon *et al.* (1977) reported an initial flux of 105-120 liters/m^2/h at 65°C with an Abcor HFJ tubular unit processing similar defatted soy flour extracts of 4.8% T.S. This compares with 38—47 liters/m^2/h obtained at 50°C with the hollow fibers

used in this study (Fig. 4 and 5). However, the Abcor unit was (presumably) operating at 60 psig while the inlet pressure of the hollow fibers was 25 psig. Based on this single point data, the tubular unit's A values are 0.26-0.29 liters/m^2/h/kPa while the hollow fiber's A values are 0.23-0.28 liters/m^2/h/kPa. Similarly, a Union Carbide UCARSEP system operating at 65°C reported an unusually high flux of 230 liters/m^2/h for 4.8% T.S. soy extracts (Lawhon *et al.* 1977). The pressure, however, was probably close to the maximum rated value of 600 psig, which would give it the low A value of 0.057 liters/m^2/h/kPa.

CONCLUSIONS

In the hollow fiber-defatted soy flour extract system studied here, permeate flux was significantly pressure and temperature dependent, but relatively independent of flow rate, within the physical constraints of the module studied. Performance characteristics were best expressed by a modified power model based on the Poiseuille equation for flow through channels. The two parameters of the model, A and n, are probably functions of osmotic pressure, temperature and membrane compaction effects. To enable a relatively unbiased comparison of different ultrafiltration units and/or feeds, it is strongly recommended that performance data be expressed in terms of these two parameters which together will uniquely characterize a particular membrane-feed combination in the pressure-controlled region.

ACKNOWLEDGMENT

Funds for this research were provided in part by the College of Agriculture Experiment Station. The Hunter-Wright Fellowship, University of Illinois and the Pillsbury Fellowship, Institute of Food Technologists, for the senior author (DJN) are gratefully acknowledged. This paper is based on a M.S. thesis submitted by DJN to the Graduate College, University of Illinois, Urbana.

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STRUCTURE EVALUATION OF FOUR DRY CRISP SNACK FOODS BY SCANNING ELECTRON MICROSCOPY

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INTRODUCTION

The structure of dry cereal-based snack foods is important with respect to perceived textural sensory characteristics. One of the major sensory properties is crispness (Nielsen 1979) which is controlled by the amount of water bound to the carbohydrate matrix. Recently Katz and Labuza (1980) reported a study on the effect of water activity on the sensory characteristics of saltines, popped popcorn, extruded corn curls and potato chips. They found that these products were perceived as becoming noncrisp, and therefore undesirable, in a critical water activity (a_w) range of 0.36 to 0.51 as seen in Table 1. This range is typical for transformation between amorphous and crystalline states of carbohydrates (White and Cakebread 1966) and for mobilization of food soluble constituents (Duckworth *et al.* 1976). Katz and Labuza (1980) also found that there was a major change in the force-deformation curves as measured by Instron analysis in this a_w range. This led to the idea that the increasing a_w, and therefore water content, acted by dissolving semi-crystalline carbohydrate zones which then swelled. This swelling decreased the crispness intensity factor as measured by Instron, and possibly should show visually observable physical changes at the ultrastructural level that could be related to crispness. Saltmarch and Labuza (1980) have recently shown, using scanning electron microscopy (SEM), that an amorphous to crystalline change in lactose occurs in whey powder between a_w 0.35 and 0.44. This change influenced both the quality and the flow properties of the powder.

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Table 1. Critical moisture content and water activity for sensory loss of crispness (from Katz and Labuza 1981)

Product	g H_2O/100 g solids	a_w
Saltine cracker	7.0	0.39
Potato chip	5.7	0.51
Puffed corn curl	4.2	0.36
Popcorn	6.1	0.49

METHODS

To determine if indeed observable structural changes took place, the four snack foods were subjected to SEM analysis. Each dry product after mounting on aluminum stubs was humidified at $a_w = 0.11$, which results in a very crisp product, and at an a_w (generally above 0.5) at which the product was perceived as being noncrisp and undesirable. The samples were then coated with gold/palladium (60%/40%) and viewed in a Phillips model 500 SEM at various magnifications with an accelerating voltage of 6 kV and a spot size between 320-640Å.

RESULTS AND DISCUSSION

Photomicrographs of a saltine cracker, potato chip and puffed corn curl at $a_w = 0.11$ and at an a_w above the point at which sensory crispness is lost are shown in Fig. 1, 2 and 3, respectively. There were no observable gross structural differences between the low a_w and high a_w for the samples. Although the high a_w sample could have lost water during the coating procedure and changed, studies by Saltmarch and Labuza (1980) with whey powders did not find this to be a problem, and thus, it was not considered here. Thus, there were no observable crystallinity changes in the carbohydrates at the ultrastructural level.

The saltine photomicrographs (Fig. 1) resemble the photomicrographs of Varriano-Marston (1977) for dough systems. The presence of platelet-shaped starch granules in the gluten matrix indicate that starch gelatinization does not occur to a great extent during the baking of saltine crackers. Furthermore, the low water content dough and short baking time seem to minimize starch gelatinization. This was also observed by Hoseney *et al.* (1977) and Lineback and Wongsrikasen

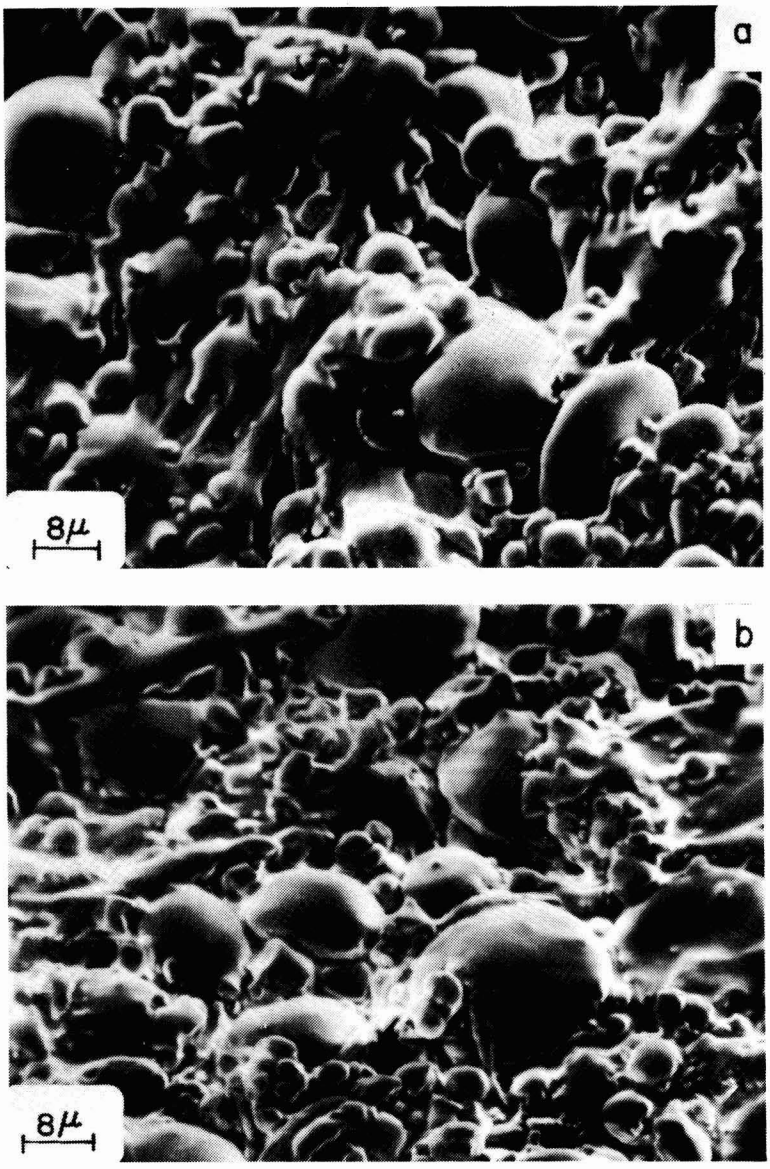

FIG. 1. SCANNING ELECTRON PHOTOMICROGRAPHS OF THE STRUCTURE OF SALTINE CRACKERS® AS A FUNCTION OF WATER ACTIVITY

a. $a_w = 0.11$, b. $a_w = 0.75$.

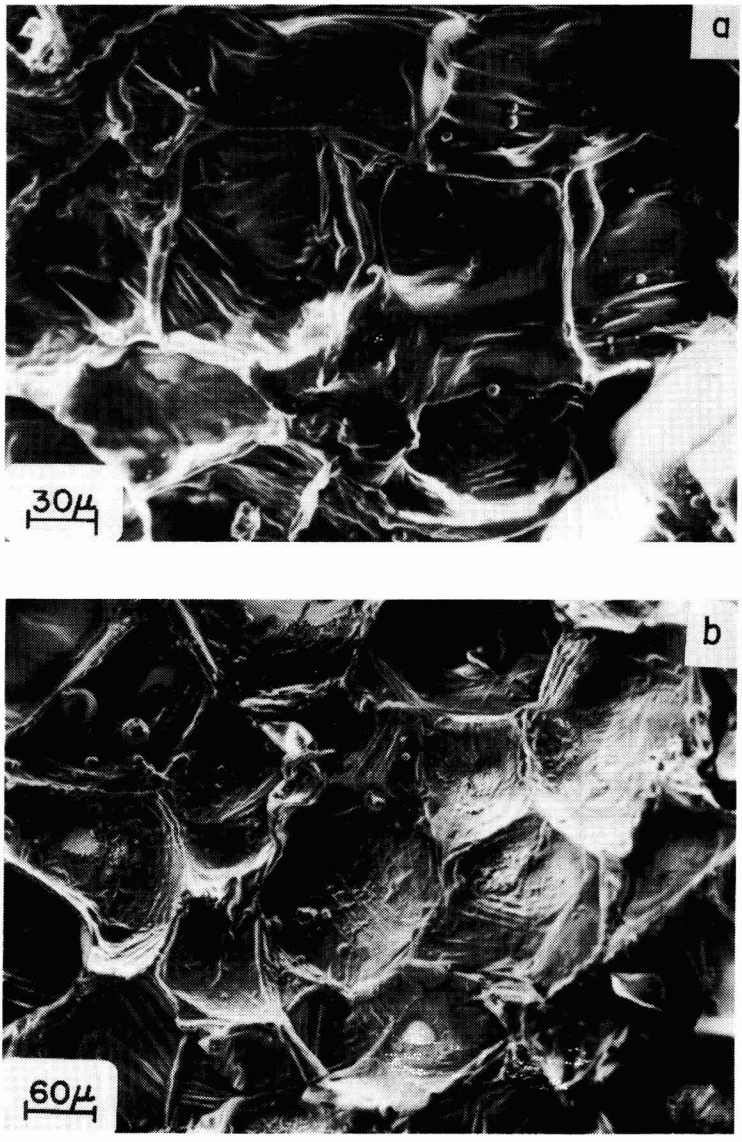

FIG. 2. SCANNING ELECTRON PHOTOMICROGRAPHS OF THE STRUCTURE OF POTATO CHIPS AS A FUNCTION OF WATER ACTIVITY

a. $a_w = 0.11$, b. $a_w = 0.75$.

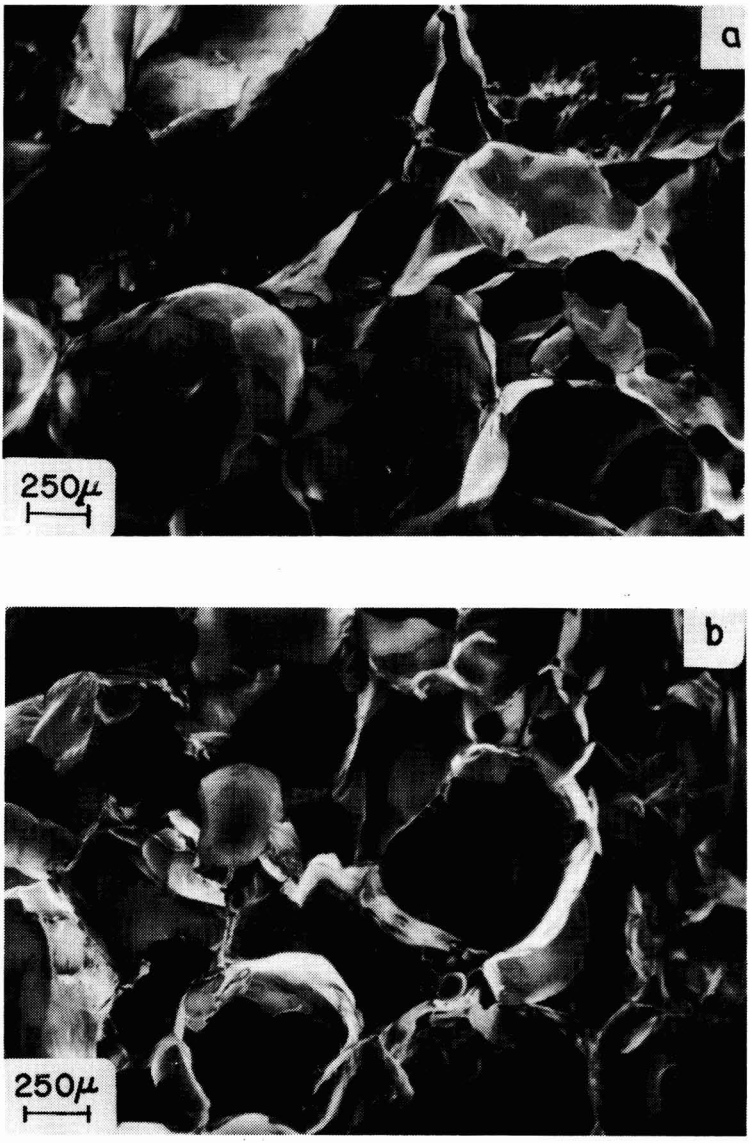

FIG. 3. SCANNING ELECTRON PHOTOMICROGRAPHS OF THE STRUCTURE OF EXTRUDED PUFFED CORN CURLS AS A FUNCTION OF WATER ACTIVITY

a. $a_w = 0.11$, b. $a_w = 0.52$.

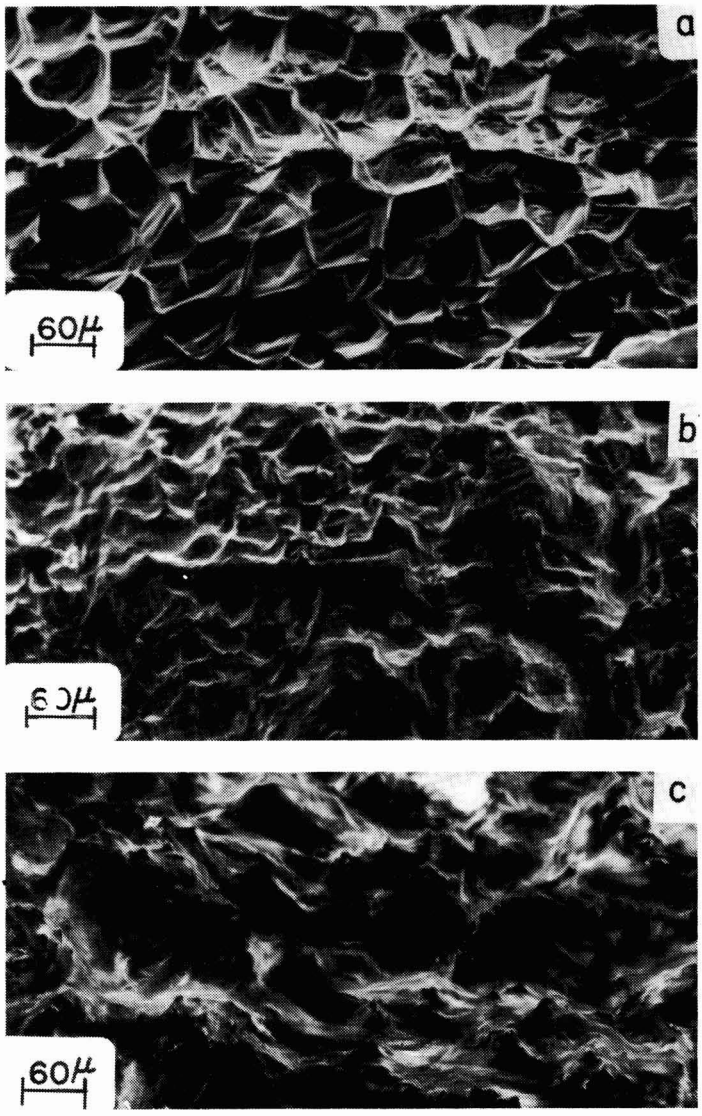

FIG. 4. SCANNING ELECTRON PHOTOMICROGRAPHS OF THE STRUCTURE OF POPCORN HUMIDIFIED TO DIFFERENT WATER ACTIVITY

a. $a_w = 0.11$, b. $a_w = 0.75$, c. $a_w = 0.85$.

(1980) for sugar cookies.

The potato chip photomicrographs (Fig. 2) show the contour of potato cells; however, starch granules are not present as was seen by

Galletti *et al.* (1980) for raw potatoes. The starch granules are either heat fixed during the deep fat frying and rupture out of the system, or are gelatinized and coat the potato cell walls. The photomicrographs of cross-sectioned puffed corn curls (Fig. 3) resemble the photomicrographs of cross-sectioned spaghetti shown by Dexter *et al.* (1978). Both of these products are extruded systems and show a honeycombed fiber network. Starch granules were not found in the puffed corn curls since they are gelatinized during the extrusion process.

A photomicrograph of a typical popcorn kernel surface at a_w 0.11 is shown in Fig. 4a. Although not shown, there were no observed structural differences between the a_w = 0.11 to 0.65. Reeve and Walker (1960) examined cross sections of popcorn and found a similar soap bubble arrangement of cells. At a_w = 0.75, popcorn begins to undergo a cellular collapse as shown in Fig. 4b, and at a_w = 0.85 the cellular arrangement is almost completely lost as seen in Fig. 4c. It is unlikely that a consumer would want to eat popcorn at this condition, since this structural transformation occurs at an a_w far above the critical value for crispness. A possible mechanism for this occurrence is that as water is absorbed by the popcorn, it softens the product and dissolves some of the intercellular glue-like material and gelatinized starch on the cell walls, and at high enough water content the cells just collapse. These results also substantiate the fact that water loss during coating is not a problem.

If no major structural changes take place in or near the critical a_w range, why then do these snack foods lose crispness? Two possibilities exist. Vickers (1975) showed that the acoustical manifestations that occurred while dry snack foods were chewed changed with a_w. She hypothesized that the presence of moisture changed the system structure in a manner which then changed the rate and magnitude of propagation of sound waves. Katz and Labuza (1980) postulated that the perception of loss of crispness was due to a dissolution and swelling of the crystalline carbohydrate zones because of more water-water and water-carbohydrate hydrogen bonds as found by differential scanning calorimetry (Suggett 1965). The amount of water that is needed to be absorbed to go from a crisp to a noncrisp state is between 1 to 3 grams per 100 grams solids, and is thus very small. The mechanism for loss in crispness must therefore occur at the molecular level since, as found in this present study, no gross macroscopic structural changes as viewed by SEM have taken place. Further work on acoustical properties and using X-ray diffraction would be needed to verify the theory.

Overall, this work and that of Katz and Labuza (1980) show that moisture protection is critical in maintaining high quality in dry crisp snack foods. This can be achieved by drying the product to lower moisture contents or by better protective packaging. The latter is preferred since, as shown by Quast and Karel (1972), if dried too low, fat-containing snack foods will become rancid very rapidly. In addition, this study shows that scanning electron microscopy should not be used alone as a tool in scientific studies of food, but that physico-chemical studies are needed to be able to draw valud conclusions.

ACKNOWLEDGMENT

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BOOK REVIEW

Food Control in Action, Edited by P. O. Dennis, J. R. Blanchfield and A. G. Ward. Applied Science Publishers Ltd., Ripple Road, Banking Essex England. 1980. 290 pp, index, 12 tables and 12 illustrations.

This book, like many now being published is a compilation of a series of lectures given at a conference complete with a text of the discussion which followed the lectures. The book provides interesting reading and gives some insight into the attitude in England towards quality control/quality assurance. In my opinion, a textbook it is not.

The initial chapter discusses the philosophy of food control quite adequately. It essentially sets the tone for the remainder of the book. The author of this chapter, J. Ralph Blanchfield points out succinctly the needs and reasons for food control and he defines food control rather broadly. For those interested in philosophy this chapter would be particularly useful.

The remainder of the book is divided into four sections or sessions. The first is concerned with the components of food control and divides these components into three, scientific basis, technological basis and methodological basis. A rather interesting section particularly when one considers the various facets that are possible with these three components.

The constraints of food control are discussed in session. From four views, the market requirements, the economic limitations, legislative problems and organizational constraints. This section provides some insight into the English concept of the limits associated with food control.

Session three discusses the interactions involved in developing and maintaining food control from raw material to ultimate consumption. This section also is divided into four parts, product/process development interface is adequately discussed by a Director of Research from an English food firm. Purchasing of materials and involvement of distribution and the consumer are two of the three remaining lectures. The fourth, probably the meat of this meeting, is devoted to discussing how quality assurance, production and productivity interact. It is an interesting view. Practical applications of food control methods are also covered in the fourth section including chocolate drops and fish fillets manufacture in this section. For those readers interested in application this section would be the most valuable.

If one is involved in marketing products in England this book might be useful, for those not so involved it would only be another book on

the shelf that has little use.

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Developments in Food Analysis Techniques - 2, Edited by R. D. King. Applied Science Publishers, Ltd., London. 1980.

This is the second volume of the Development Series in Food Analysis. The purpose of this series is to examine, in detail, some of the current techniques in food analysis. Each chapter is a comprehensive review of the subject. This volume contains chapters on texture measurement (by J. G. Brennen), determination of food colors (by R. D. King), fluorometric methods (by J. W. Bridges), optical microscopic methods (by E. C. Apling) determination of food lipids (by Hitchcock and Hammond) and determination of vegetable proteins in meats (by Olsman and Hitchcock).

The chapter on food texture covers the literature from 1925 to 1979 and contains 278 references. The methods reviewed include sensory, instrumental, sonic, structural examination, chemical analytical and a catch-all, miscellaneous methods.

The determination of food colours includes a discussion of surface appearance as quantified by CIE tristimulus values and the CIE-Lab system. Methods are presented for the quantification of synthetic colours in foods by TLC, paper chromatography and HPLC. There is a section on natural food colours however, this discussion is rather brief.

The chapter on fluorometric techniques covers the subject very broadly. References are given for the analysis of food additives, vitamins carbohydrates, lipids, proteins, enzymes, pigments, food contaminants and adulterants and minerals via fluorometric techniques. A brief discussion of some of the methods is also presented.

The chapter on the optical microscope in food analysis was particularly fascinating since I have never been exposed to this subject other than for the determination of filth in foods. Dr. Apling covers the subject in a broad sense indicating the capabilities and *limitations* of this method. He deals with the quantitative and qualitative analysis of food component via microscopy. This chapter is intended as an introduction to the subject with adequate references to lead the reader into the technique. The chapter on lipids covers some of the newer techniques of lipid analysis. The authors present substantial information which is not in print and, therefore, goes well beyond the typical review article. The analysis of lipids (including vitamins) via TLC, GC

and HPLC is emphasized. A final section on problems associated with the measurement of lipid deterioration is also included.

Olsman and Hitchcock review the determination of vegetable proteins in meat products. Their discussion focuses on the determination of soy in meat. A small section is devoted to the detection of other vegetable proteins in foods but is quite limited in scope. Methods for soy protein based on microscopy, histology, electrophoresis, immunology and chromatography are described and discussed.

The book, as a whole, is well written. The information is current and complete. Each subject is covered in detail by an expert. The book is a very valuable asset to anyone involved in any of the areas of food analysis presented in this volume.

GARY A. REINECCIUS
UNIV. OF MINNESOTA

MEETING

FOCUS ON FOOD SCIENCE SYMPOSIUM III

Modern Meat Technology — Microbial Considerations

September 25, 1981. Kansas State Union, Kansas State University, Manhattan, Kansas 66506 USA.

Program

Morning Session: K-State Union

Presiding: Dr. D. Y. C. Fung

8:30 Registration, Coffee
9:15 Opening Remarks:
9:20 Principles and Practices of Modern Meat Processing
10:00 Storage and Shelf-life of Meat Processed Using Modern Technology

Coffee

11:00 Meat Microbial Quality Assurance — A retailer's approach
11:30 Home Meat Preservation — Cautions and Concerns
12:00 Luncheon: Cottonwood Room, K-State Union

Afternoon Session: K-State Union

Presiding: Dr. C. L. Kastner

1:45 Microbiology of Electrically Stimulated, Hot-boned, Vacuum Packaged Beef
2:15 Microbiology of Vacuum Packaged Pork
2:45 Microbiology of Poultry and Fish
3:15 Emerging Technology for the Extension of Meat Shelf-life
4:00 Announcements and Adjournment

Further Information

Questions concerning the Symposium should be directed to Dr. D.Y.C. Fung, Co-Chairman (913) 532-5654 or Dr. C. L. Kastner, Co-Chairman (913) 532-6131. Mailing Address: Call Hall, KSU, Manhattan, Kansas 66506 USA.

GUIDE FOR AUTHORS

Typewritten manuscripts in triplicate should be submitted to the editorial office. The typing should be double-spaced throughout with one-inch margins on all sides.

Page one should contain: the title, which should be concise and informative; the complete name(s) of the author(s); affiliation of the author(s); a running title of 40 characters or less; and the name and mail address to whom correspondence should be sent.

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

The main text should begin on page three and will ordinarily have the following arrangement:

Introduction: This should be brief and state the reason for the work in relation to the field. It should indicate what new contribution is made by the work described.

Materials and Methods: Enough information should be provided to allow other investigators to repeat the work. Avoid repeating the details of procedures which have already been published elsewhere.

Results: The results should be presented as concisely as possible. Do not use tables *and* figures for presentation of the same data.

Discussion: The discussion section should be used for the interpretation of results. The results should not be repeated.

In some cases it might be desirable to combine results and discussion sections.

References: References should be given in the text by the surname of the authors and the year. *Et al.* should be used in the text when there are more than two authors. All authors should be given in the References section. In the Reference section the references should be listed alphabetically. See below for style to be used.

DEWALD, B., DULANEY, J. T. and TOUSTER, O. 1974. Solubilization and polyacrylamide gel electrophoresis of membrane enzymes with detergents. In *Methods in Enzymology*, Vol. xxxii, (S. Fleischer and L. Packer, eds.) pp. 82–91, Academic Press, New York.

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

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

Journal abbreviations should follow those used in *Chemical Abstracts*. Responsibility for the accuracy of citations rests entirely with the author(s). References to papers in press should indicate the name of the journal and should only be used for papers that have been accepted for publication. Submitted papers should be referred to by such terms as "unpublished observations" or "private communication." However, these last should be used only when absolutely necessary.

Tables should be numbered consecutively with Arabic numerals. The title of the table should appear as below:

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

Description of experimental work or explanation of symbols should go below the table proper.

Figures should be listed in order in the text using Arabic numbers. Figure legends should be typed on a separate page. Figures and tables should be intelligible without reference to the text. Authors should indicate where the tables and figures should be placed in the text. Photographs must be supplied as glossy black and white prints. Line diagrams should be drawn with black waterproof ink on white paper or board. The lettering should be of such a size that it is easily legible after reduction. Each diagram and photograph should be clearly labeled on the reverse side with the name(s) of author(s), and title of paper. When not obvious, each photograph and diagram should be labeled on the back to show the top of the photograph or diagram.

Acknowledgments: Acknowledgments should be listed on a separate page.

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

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

EDITORIAL OFFICE: Prof. T. P. Labuza, Editor, Journal of Food Processing and Preservation, University of Minnesota, Department of Food Science and Nutrition, Saint Paul, Minnesota 55108 USA

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