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Journal of FOOD PROCESSING and PRESERVATION

Edited by
T.P. LABUZA

FOOD & NUTRITION PRESS, INC.
WESTPORT, CONNECTICUT 06880
USA

VOLUME 7, NUMBER 3 1983

JOURNAL OF FOOD PROCESSING AND PRESERVATION

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All subscriptions and inquiries regarding subscriptions should be sent to Food & Nutrition Press, Inc. P.O. Box 71, Westport, Connecticut 06881 USA.

One volume of four issues will be published annually. The price for Volume 7 is $65.00 which includes postage to U.S., Canada, and Mexico. Subscriptions to other countries are $77.00 per year via surface mail, and $85.00 per year via airmail.

Subscriptions for individuals for their own personal use are $45.00 for Volume 7 which includes postage to U.S., Canada, and Mexico. Personal subscriptions to other countries are $57.00 per year via surface mail, and $65.00 per year via airmail. Subscriptions for individuals should be sent direct to the publisher and marked for personal use.

The *Journal of Food Processing and Preservation* is listed in *Current Contents/ Agriculture, Biology & Environmental Sciences (CC/AB).*

The *Journal of Food Processing and Preservation* (ISSN: 0145-8892) is published quarterly by Food & Nutrition Press, Inc.—Office of Publication is 155 Post Road East, Westport, Connecticut 06881 USA. Current issue is September 1983.

Second class postage paid at Westport, CT 06881.

POSTMASTER: Send address changes to Food & Nutrition Press, Inc., P.O. Box 71, Westport, CT 06881.

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FOOD & NUTRITION PRESS, INC.
WESTPORT, CONNECTICUT 06880 USA

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ISSN 0145-8892

Printed in the United States of America

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MEETING

Kansas State Offers Rapid Methods Workshop

An eight-day intensive workshop on rapid methods and automation in microbiology will be held at Kansas State University July 14-21, 1984.

The workshop, directed by Dr. Daniel Y. C. Fung, an internationally known scientist in this area, will provide hands-on experience in the rapidly developing field of automated instrumentation and diagnostic kits in applied microbiology.

More than 15 companies will participate in the workshop and will provide the newest instruments and kits for students to use in working with these modern systems. In addition, Dr. Nelson A. Cox of Russell Research Center, Athens, Georgia, and Dr. Millicent C. Goldschmidt of the University of Texas will present lectures in diagnostic kits and automated instrumentations.

The course will carry 7.2 Continuing Education Credits of the American Society for Microbiology. Interested persons should contact Dr. Daniel Y. C. Fung at Call Hall, Kansas State University, Manhattan, KS 66506 or call (913) 532-5654.

PREPARATION, ULTRASTRUCTURE, AND FUNCTIONAL PROPERTIES OF EGG ALBUMIN AND CORN ZEIN MODIFIED VIA THE PLASTEIN REACTION

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Received for Publication June 15, 1983

ABSTRACT

Scanning Electron Microscopy (SEM) was used to study changes during the preparation of plasteins from egg albumin and corn zein protein isolates. This included an examination of protein particles that had been spray-dried, freeze-dried, hydrolyzed, and synthesized into plastein reaction products. Water holding capacity, oil binding capacity, and gel strength properties before and after modification are discussed. The study demonstrated that the quantity and quality of plastein products are dependent upon both the substrate and the enzyme used. A possible relationship is proposed between ultrastructural characteristics and actual functional performance of unmodified and modified proteins.

INTRODUCTION

Proteins can be modified by either chemical or enzymatic treatment (Feeney and Whitaker 1977). Presently, methods are being investigated to modify unconventional and novel proteins so as to make their incorporation into food systems attractive to the consumer. Examples of such proteins are fish protein concentrate, leaf protein concentrate, corn zein, and others that lack the functional and sensory attributes needed for human food consumption.

Recent attention has been directed toward increasing the utilization of these proteins by enzymatic modifications via the plastein reaction (Arai *et al.* 1975; Eriksen and Fagerson 1976; v. Hofsten and Lalasidis 1976). The plastein reaction is an enzymatic process by which proteins can be modified, to change their functional, sensory and nutritional properties

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(Arai *et al.* 1975). But, before the plastein reaction can be utilized outside laboratory conditions, more information is needed regarding the factors affecting quality and quantity of the plasteins formed. The objective of this study was to prepare and compare production of plasteins using egg albumin and corn zein, and to characterize their modified products using the scanning electron microscope (SEM) and selected functional tests.

EXPERIMENTAL

Materials

Egg albumin preparation and corn zein preparation were obtained from ICN Pharmaceuticals, Inc., Cleveland, OH.

Enzymes used were: pepsin (3X crystallized, hog stomach mucosa), alpha-chymotrypsin (3X crystallized beef pancreas) from ICN Pharmaceuticals, Inc., molsin (Lot No. 500033), Cal. Biochem., San Diego, California, and trypsin (1:300) (Lot No. 81442), General Biochemicals, Charagrin Falls, OH.

L-cysteine (free base) obtained from Nutrition Biochemicals Corporation was used as a papain activator in a 0.01 M concentration.

All other chemicals were reagent grade.

Methods

Solubilization of Egg Albumin and Corn Zein. The suspensions of egg albumin and corn zein (1% w/v) were adjusted with 2N HC1 to a test pH of 1.6. The suspensions were then brought to 37°C and pepsin was added at a ratio of E/S = 1/100. The suspensions were agitated at 37°C for 24 h. During the course of digestion, pH changes were very slight ($\leq \pm$ 0.3 pH units). At this time the suspension was readjusted to pH 7.

General Preparation of Plasteins. Suspensions of pepsin hydrolysates of zein and egg albumin were then freeze-dried (Virtis Co., Inc., Gardiner, N. Y.) at room temperature and 100 μHg for 72 h. The powder was then reconstituted to a 40% suspension (w/v). The pH was adjusted to 5.0 with 2N NaOH and brought to 37°C. A second proteolytic enzyme was then added at (E/S = 1/100) (either pepsin, alpha-chmotrypsin, molsin, or papain). A gel usually formed in one hour or less. After 24 h the reaction was stopped by raising the temperature to 80°C to inactivate the enzyme. The plastein reaction product was then freeze-dried using the same conditions as above or it was used directly in some tests.

Measuring Plastein Formation and Water Insoluble Material Production. Freeze-dried plastein reaction mixtures were fractionated

by suspending 1.0 gram of dry material in 100 ml of 10% (w/v) trichloroacetic acid or distilled water followed by centrifugation at 38,000g for 30 min at 5°C. The insoluble fraction in the TCA solution has been defined as the "plastein fraction" by Yamashita *et al.* (1970). The supernatant contained the soluble peptides or the "non-plastein material".

The change in water insoluble material was monitored by measuring the disappearance of aromatic amino acids from the supernatant (using absorption @ 280 nm) and comparing to respective hydrolysate solutions. In addition the weight of the precipitate after centrifugation as compared to the total hydrolysate weight was determined (% production of plastein). This was corrected for the amount of precipitate formed by the hydrolysate itself.

Sample Preparation for Scanning Electron Microscopy (SEM). For the SEM studies the original protein and the freeze-dried preparations were fractured and dusted onto aluminum stubs prepared with silver paint (GE Electronics, Rockford, Ill.). These were sputter coated with gold in a Hummer Diode Sputtering Coater (Technics Corporation, Alexandria, VA) fitted with a cooling stage. The specimens were then viewed in a AMR100 Scanning Electron Microscope at 10-20 KV.

Water Holding Capacity (WHC). Water holding capacity was determined by a slight modification of the method of Lin *et al.* (1974). One gram samples (freeze dried) were added to test tubes (15mm x 125mm) and the test tubes were weighed. Ten milliliters of distilled water was then added and the samples were agitated, brought to 25°C and held for 1 h with vortexing for 5 s every 15 min. The samples were then centrifuged at 1600g for 25 min and the supernatant liquid was poured into graduated cylinders and the volume was measured. The samples were then inverted at a 45° angle and allowed to drain onto absorbent toweling for 30 min. Tubes were reweighed and differences between dry weight and wet weight of samples calculated. Values of WHC are reported as percent increase in weight of the dry sample.

Oil Binding Capacity. Oil binding capacity was determined by a modification of the method of Lin *et al.* (1974). One gram quantities were weighed into (15mm x 125mm) test tubes. Six milliters of peanut oil were added to each of the samples and the tube was agitated for 1 min on a vortex. The samples were allowed to react at 25°C for 1 h with agitation every 15 min for 5 s. The samples were then centrifuged for 25 min at 1600g. The tubes were inverted at a 45° angle and allowed to drain onto paper toweling for 30 min. Oil binding values were reported as ml of oil bound/gram of sample.

Gel Strength Index Determination. The Instron Universal Testing Machine Model #TM (Instron Corp., Canton, MA) was used to perform

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puncture tests on plastein gel surfaces. The force level required to reach the yield point, (the force at which the metal probe begins to penetrate the product) was taken as an index of gel strength. Plastein gels were prepared in 100 ml beakers to give a final volume of approximately 15 ml. Measurements were made with the compression load cell CB (Instron Corp.), ¼ in. drive pin punch (L.S. Starret Co., Athol, MA) drive speed 2 in./min, chart speed 10 in./min, and full scale load of 0-50 g, 0-500 g) or 0-2000 g as required. Five punctures were made on each gel surface and the average yield point value was determined. The yield point was taken as that force level at which an abrupt change in slope versus distance curves occurred.

RESULTS AND DISCUSSION

Pepsin was found to be the best enzyme for plastein production as seen in Table 1. Therefore, it was chosen as the synthesizing enzyme for plastein formation in the continuing studies dealing with ultrastructure and selected functional properties.

Table 1 shows a comparison of the plastein production by four enzymes. As seen, the plastein production depends on both the substrate and the synthesizing enzyme in addition each enzyme reduced the amount of soluble material which was greater than the percentage yield of plastein. This suggests that a larger percentage of the aromatic amino acids were incorporated into the plastein which is in agreement with Yamashita and coworkers (1970). They found that plasteins generally were enriched with aromatic amino acids.

Table 1. Comparison of plastein production by four enzymes using the TCA precipitation procedure

Enzyme	Egg Albumin		Corn Zein	
	% Production	% Decrease in Soluble Material (@ 280 nm)	% Production	% Decrease in Soluble Material (@ 280 nm)
Pepsin	44	51	37	48
alpha-chymotrypsin	31	40	27	36
Molsin	23	34	21	33
Trypsin	14	31	9	28

Although the trichloroacetic acid procedure has generally been used for measuring plastein yield, TCA would not be practical in preparing plastein reaction material for food use. Consequently, it was decided to separate the plastein from non-plastein material by centrifugation to remove

the water insoluble material. Changes in the 280 nm absorbing material were measured in the supernatant as had been done with the TCA precipitation method, and the water insoluble material weighed. In general, the results shown in Table 2 are similar to those in Table 1. They indicate that the reduction in soluble aromatic amino acids exceeds the increase in yield of water insolubles. As seen in Table 2, the decrease in soluble material (@ 280 nm) for corn zein is slightly greater than the values for egg albumin probably because zein has more aromatic amino acids. However, the yields of insoluble material for the egg albumin were higher except for the pepsin treated zein. If ultrafiltration or dialysis with water were to be utilized on an industrial scale for plastein production improved characterization or a redefining of the products produced will be needed.

Table 2. Comparison of water insoluble material produced by the plastein reaction using four enzymes

	Egg Albumin		Corn Zein	
Enzyme	% Production	% Decrease in Soluble Material (@ 280 nm)	% Production	% Decrease in Soluble Material (@ 280 nm)
Pepsin	30	48	44	63
alpha-chymotrypsin	24	35	19	38
Molsin	21	28	16	35
Trypsin	18	27	11	29

The ultrastructure and the functional properties were investigated using SEM and selected functional tests using the plastein gels utilizing pepsin as the synthesizing enzyme. Table 3 lists some of the functional properties of albumin and zein hydrolysates and their respective modified products. The water holding capacity (WHC) or the percentage water bound was increased in comparing incubation times of 15 min versus 24 h. The increase was over 3 fold for albumin and 10 fold for zein. The centrifugation method for separation yielded a product with a two fold increase in WBC for both plasteins and a 50 to 70% increase in OBC for albumin and zein, respectively. The mechanism of action of TCA on "proteins and protein-like material" products such as plastein products is unknown at this time but it is possible that the TCA action contributes to the observed differences. For the plastein reaction gel product itself as the albumin was much weaker than that from zein.

Figure 1 shows a scanning electron micrograph of spray-dried egg albumin. The particles are smooth, dimpled spheres which are probably caused by atomization of the protein solution during spray-drying. The physical process of spray drying affects the functional properties of egg albumin by

Table 3. Functional properties of egg albumin, corn zein and their modified products

	WHC (% Water Bound)	Gel Strength	OBC (ml of Oil/g)
Freeze-dried albumin	a	b	4.7
Albumin hydrolysate	a	b	3.2
Zein hydrolysate	a	b	2.7
15 min albumin plastein reaction products	40	no gel	1.2
15 min zein Plastein reaction products	12	194	1.1
24 h albumin plastein reaction products	124	16	1.5
24 h zein plastein reaction products	120	290	1.3
TCA insoluble albumin plastein	151	b	1.9
TCA insoluble zein plastein	97	b	1.4
Water insoluble albumin plastein	349	b	2.8
Water insoluble zein plastein	176	b	2.4

a. No value obtained
b. Test not applicable

producing very fine particles. If spray-dried albumin is dissolved in water and freeze-dried, large jagged, thin sheets are obtained as shown in Fig. 2b. When these flat sheets (Fig. 2b) were exposed to enzymatic hydrolysis the size was changed (Fig. 3a). These large and small particles have been separated in our laboratory by ultrafiltration.

Figure 3b shows the freeze-dried plastein gel of egg albumin. Plastein gel appear sponge-like and rough in appearance, while the hydrolysates are thin and sheet like (Fig. 3a). In Fig. 4a sheets of the zein hydrolysate are evident. The spongy character of the plastein reaction products from zein is evident in Figure 4b and is typical of most gels. The larger holds may be due to gas incorporation as suggested by Geil-Hansen and Flink (1976). These SEMs appear to support and agree with the water holding capacity and gel strength data.

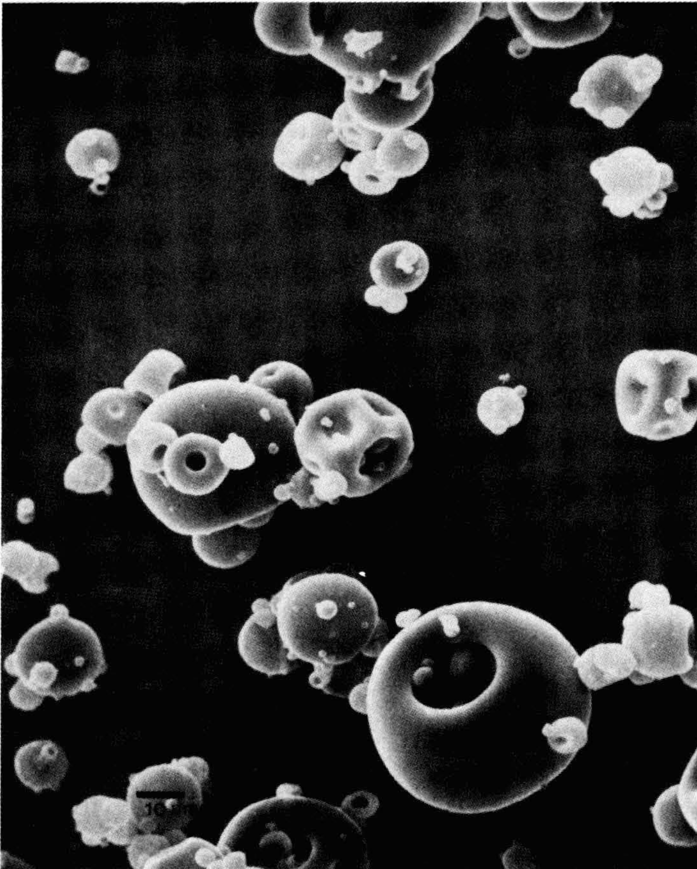

FIG. 1. SCANNING ELECTRON MICROGRAPH OF NATIVE SPRAY DRIED EGG ALBUMIN (ICN PHARMACEUTICALS, CLEVELAND, OHIO).

In summary, this study, has demonstrated that the quantity and quality of the plastein products are dependent upon the substrate, enzyme, and fractionation technique (method for separating soluble from insoluble material). The ultrastructure studies indicated that scanning electron microscopy can provide a potentially useful technique for observing changes of proteins modified by physical or enzymatic processes. Still, further studies are needed to elucidate the mechanism of the plastein reaction. A clear understanding of the plastein formation mechanism is essential if plasteins are to be generated with defined functional properties.

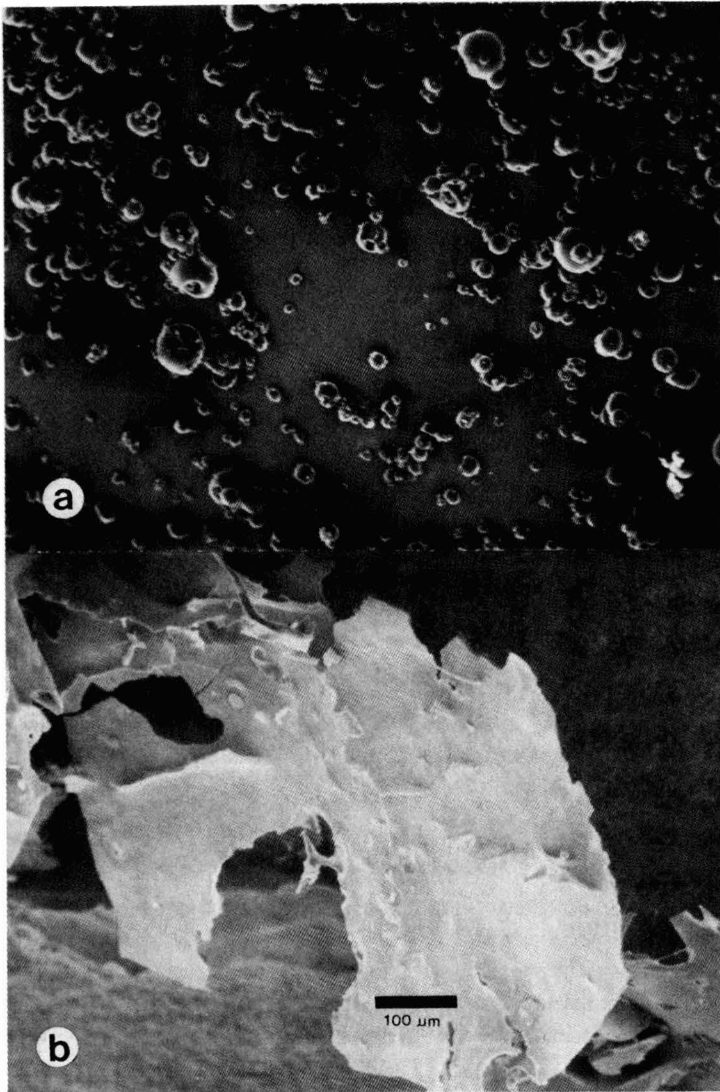

FIG. 2. COMPARISON BETWEEN SCANNING ELECTRON MICROGRAPHS OF COMMERCIALLY SPRAY DRIED AND LABORATORY FREEZE DRIED EGG ALBUMIN

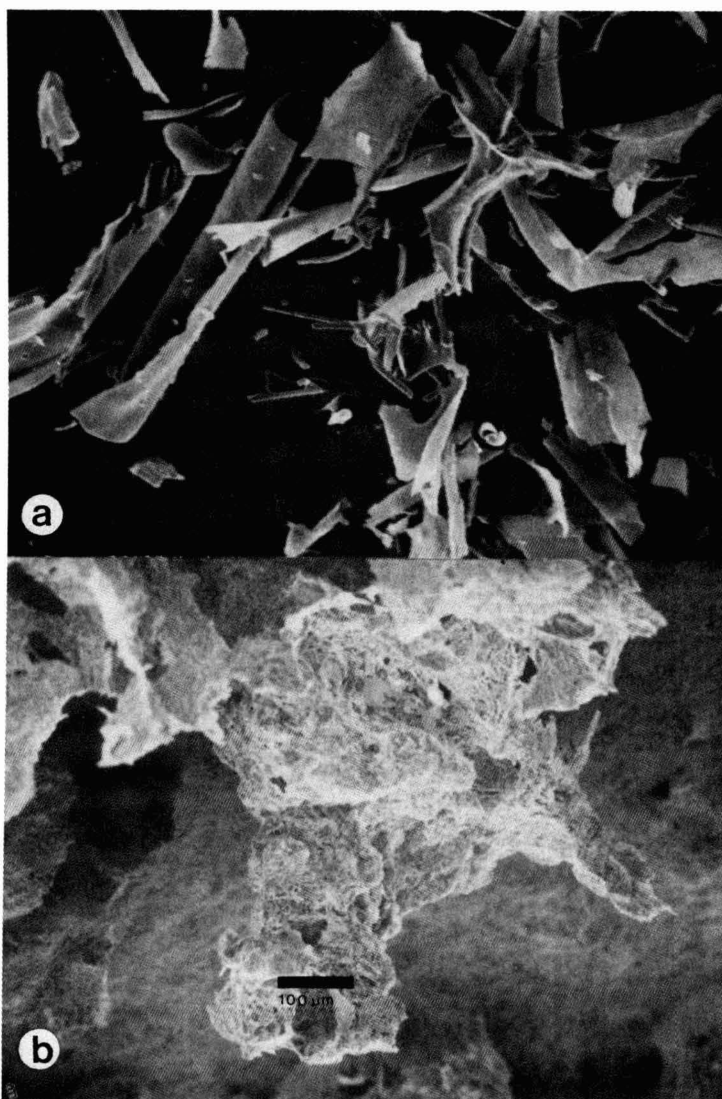

FIG. 3. SCANNING ELECTRON MICROGRAPHS OF HYDROLYZED COMMERCIAL ALBUMIN AND SAME MATERIAL AFTER PEPSIN EGG PLASTEIN REACTION

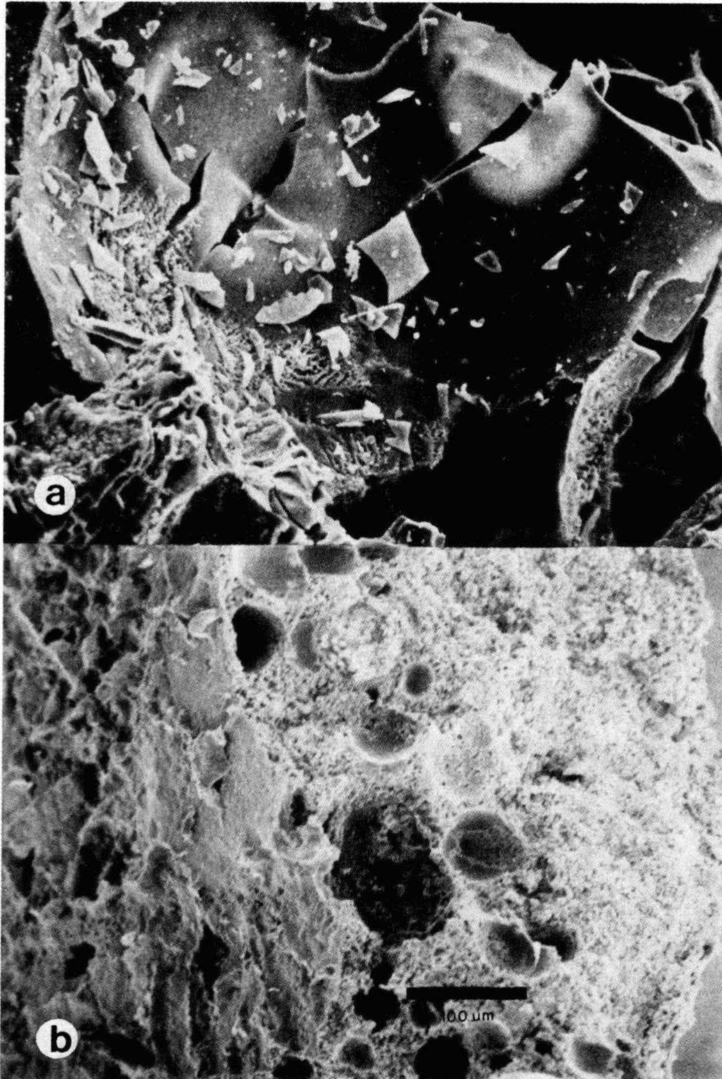

FIG. 4. SCANNING ELECTRON MICROGRAPHS OF HYDROLYZED COMMERCIAL CORN ZEIN AND SAME MATERIAL AFTER PEPSIN PLASTEIN REACTION

ACKNOWLEDGMENTS

The authors acknowledge the financial support from USDA Hatch Funds of the New York State Experimental Station.

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VARIETAL DIFFERENCES IN CHEMICAL CHARACTERISTICS RELATED TO COOKING QUALITY OF COWPEA

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Received for Publication February 25, 1983
Accepted for Publication July 12, 1983

ABSTRACT

Thirteen cowpea varieties were tested for soaking rate and cooking quality. The rate of water imbibition was not related to cooking time. Cooking time varied between 41.5 and 135 min. Cooking resulted in losses of 5.2-69.5% for calcium, 13.9-33.3% for magnesium, 12.6-22.2% for phytic acid and 45.7-63.1% for pectin. Among the chemical characteristics measured, only phytic acid content was moderately correlated with cooking time.

INTRODUCTION

Legumes constitute the major sources of plant proteins in human diets. Among them is the cowpea which is widely eaten in many parts of the world. One notable feature of the cowpea and other beans is that certain cultivars take a longer time to soak or cook than others thereby creating preferential acceptance by consumers regardless of nutritive value of the cultivar. Among other factors, the cooking quality of legumes is affected by varietal differences, time of storage and processing (Muller 1967; Burr *et al.* 1968 and Kumar *et al.* 1978). Some chemical characteristics of certain beans have also been clearly implicated in poor cooking quality- Rossenbaun and Baker (1969); Kon (1979); Kon and Sanshuck (1981). The purpose of the present study is to provide information on the qualities of some cowpea varieties that may help in their selection and development. Changes that occur in their chemical characterisitics on cooking are provided.

MATERIALS AND METHODS

Thirteen cowpea (*Vigna unguiculata*) varieties with average moisture content of 10.6% were obtained from the National Cercal Research Institute, Ibadan, Nigeria.

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The carbohydrate constituents of some of the varieties have been reported (Longe 1980). The dry bean seeds were ground in a Cross-Beater Laboratory mill for chemical analysis. Beans were cooked for the determined cooking periods for each variety, drained and dried before milling as for uncooked samples.

Water Imbibition

The amount of water imbibed was determined by soaking 30g samples of beans in distilled water at room temperature for periods of 4, 8, 12, 16, 18, 20, 22 and 24 h at a bean-water ratio of 3:10. The beans were removed from the water after the specified time, drained and spread over paper towels to remove excess water and reweighed.

Estimation of Cooking Time

Seeds were cooked in six times their weight of distilled water and while being cooked, samples were withdrawn and evaluated by a panel for cookability and softness (Kumar *et al.* 1978). Cooking time was therefore estimated subjectively by taking the mean of ten independent replicates.

Quantitative assays of calcium and magnesium were made after wet-ashing of uncooked and cooked samples with nitric acid, perchloric and sulphuric acids, followed by quantitative measurement in a Perkin-Elmer atomic absorption spectrophotometer. Total phosphorous was measured by the Allen (1940) method while phytic acid phosphorus was determined by the method of Young and Greaves (1953). The free pectin was quantified according to the procedure of Dietz and Rouse (1953), the anhydrouronic acid of which was estimated by the carbazole method of McComb and McCready (1952).

RESULTS AND DISCUSSION

Maximum imbibition occured between 16-18 h after which it remained constant but for a few varieties such as Farin Juda C Tvu 4551 and Nig. B.7 which reached the peak of imbibition within 4 to 8 h.

In all cases over half of the total imbibed water was absorbed by the fourth hour when the first measurement was taken (Table 1). Water imbibed could be related to the hardening of the testa as suggested by Quenzer *et al.* (1978). The amount of water imbibed in 4 h ranged from 18.1g for Farv - 13 to 33.3g for Nig. B7. For processing, varieties which were fully imbibed within the shortest possible time might be more desirable for tenderness of product.

Table 1. Water imbibition (g) cowpea varieties

Variety	Hours of Soaking							
	4	8	12	16	18	20	22	24
New Era	24.7	25.6	28.2	29.1	29.7	30.1	30.0	30.2
Farin Juda C	30.7	30.4	30.5	30.3	30.3	30.1	30.3	30.4
West bred	29.3	31.3	31.5	32.3	32.7	31.7	31.8	31.8
Nig. B4	29.4	29.5	31.8	32.4	31.7	31.7	31.6	31.4
Nig. A 10A	29.3	31.3	31.4	31.6	32.4	32.1	31.5	31.2
Nig. B7	33.3	32.0	32.1	32.3	32.4	32.8	32.8	32.7
Kano 1696	30.5	30.9	31.5	31.9	32.3	30.3	30.3	30.2
Farv 13	18.1	18.3	28.9	30.6	31.4	31.8	32.8	32.8
Line 7	22.7	23.1	23.3	24.4	24.5	24.6	24.3	24.2
Anna	24.9	25.6	25.8	26.2	27.4	29.5	27.2	28.0
Kudi	24.1	24.3	25.3	26.0	26.0	26.6	27.5	29.5
Ayi	22.2	24.4	28.5	28.8	29.0	29.0	28.9	29.1
Tvu 4557	28.3	28.4	28.5	28.7	28.8	28.2	28.2	28.1

Soaking time was not correlated with cooking time. The samples that imbibed the larger volumes of water were not necessarily cooked in shorter periods substantiating the reports of Burr *et al.* (1968) and Molina *et al.* (1976). Jackson and Varriano-Marston (1981), Varriano-Marston and Jackson (1982) also showed that hardshell is not necessarily related to the 'hard-to-cook' phenomenon. This suggests that chemical processes involved in softening of beans during soaking and cooking are not likely the same as explained by Burr *et al.* (1968). Cooking time (Table 2) was infact shortest (41.5 min.) for Ayi, one of the slower imbibers. Westbred was the most difficult to cook (135 min). Average cooking time for all varieties was 74.5 min. Kumer *et al.* (1978) reported a cooking time for cowpea of 30.6 min which increased to 60.4 min with germination compared with 13.6 and 79.0 min for germinated green gram and chick pea, respectively.

Table 2. Cooking time (min) of cowpea varieties

Variety	Cooking Time
New Era	99.5
Farin Juda C	67.0
Westbred	135.0
Nig. B4	55.0
Nig. A 10A	51.5
Nig. B7	71.0
Kano 1696	64.0
Farv 13	103.0
Line 7	86.0
Anna	59.0
Kudi	80.0
Ayi	41.5
Tvu 4557	55.5
Mean	74.5
SD	±25.9

The means and standard deviations for calcium and magnesium contents in raw and cooked samples are shown in Table 3. Magnesium contents varied between 124 and 192 mg/100g whereas calcium varied between 58 and 74 mg/100g with a standard deviation of 5.1mg. Ranges in percentage losses during cooking were 5.2 to 69.5% for calcium and 13.9 to 33.3% for magnesium.

The phytic acid content of raw cowpeas varied among varieties from 280mg/100g for New Era to 792mg/100g for Ayi. These were correspondingly reduced to 220mg/100g and 676 mg/100g in cooked samples. Phytic acid losses during cooking ranged from 12.6 to 22.21% (Table 4). Phytic acid phosphorous ranges were 79 to 223mg/100g for uncooked and 62 to 190mg/100g in cooked samples. The percentage of phytic acid to total phosphorous ranged from 19.6 to 56.7%.

Table 3. Calcium, magnesium and free pectin in cowpea varieties (mg/100g dry wt. basis)

Variety	Calcium			Magnesium			Free Pectin		
	Uncooked	Cooked	% Loss on Cooking	Uncooked	Cooked	% Loss on Cooking	Uncooked	Cooked	% Loss on Cooking
New Era	74	48	35.1	131	106	19.1	935	345	63.1
Farin Juda C	61	54	11.5	152	126	17.1	1582	718	54.6
Westbred	58	55	5.2	176	142	19.3	784	405	48.3
Nig. B4	70	45	35.7	124	96	22.6	906	415	54.2
Nig. A104	67	49	66.3	192	128	33.3	386	186	51.8
Nig. B7	70	32	69.5	140	108	22.9	482	215	55.4
Kano 1896	69	47	32.1	162	118	27.2	975	380	59.5
Farv 13	64	53	17.2	180	135	25.0	825	350	57.6
Line 7	62	40	35.6	144	124	13.9	985	400	59.4
Anna	72	59	18.2	176	131	25.6	682	370	45.7
Kudi	70	47	32.9	124	98	21.0	990	395	60.1
Ayi	65	49	24.6	160	128	20.0	1135	482	57.5
Tvu 4557	59	48	18.6	132	110	16.7	582	242	58.4
Mean	66.2	48.2	31.0	153.3	119.2	21.8	865.3	377.2	55.8
SD	±5.1	±6.9	±19.1	±22.9	±14.5	±5.1	±307.3	±133.3	±4.9

Table 4. Phytic acid and phosphorous in cowpea varieties (mg/100g dry wt. basis)

Variety	Total Phosphorous			Phytic Acid			Phytic Acid Phosphorous		Phytic Acid Phosphorous / Total Phosphorous	
	Uncooked	Cooked	% Loss on Cooking	Uncooked	Cooked	% Loss on Cooking	Uncooked	Cooked	Uncooked	Cooked
New Era	403	383	5.0	280	220	21.4	79	62	19.6	16.2
Farin Juda C	457	432	5.4	649	549	15.4	183	155	40.1	35.9
Westbred	396	376	5.1	418	340	18.7	118	96	29.8	25.6
Nig. B4	413	400	3.1	580	507	12.6	163	143	39.4	35.8
Nig. A104	400	383	4.3	660	565	14.4	186	159	46.5	41.5
Nig. B7	383	378	1.3	539	438	18.7	152	123	39.7	32.3
Kano 1696	403	399	1.0	565	470	16.8	159	132	39.4	33.1
Farv 13	440	420	4.5	411	330	19.7	116	94	26.4	22.4
Line 7	473	462	2.3	459	359	21.8	129	101	27.3	21.9
Anna	453	440	2.9	575	480	16.5	162	135	35.7	30.7
Kudi	450	360	20.0	522	406	22.2	147	115	32.7	31.9
Ayi	393	383	3.3	792	676	14.6	223	190	56.7	50.0
Tvu 4551	382	361	5.4	490	418	14.7	138	118	36.1	32.7
Mean	418.9	398.0	4.9	533.9	442.9	17.5	150.4	124.8	36.1	31.6
SD	±31.00	±31.59	±4.8	±129.5	±118.6	±3.2	±36.4	±33.2	±6.5	±8.8

The mean value for free pectin in uncooked beans was 865mg/100g. The contents of free pectin were poorly correlated with cooking time and losses as high as 63.1% were incurred during cooking.

Among the chemical parameters measured above only phytic acid was correlated with cooking time (r = 0.78). This is in agreement with the observations of Mattson (1946) and Kumar *et al.* (1978) although Mattson (1946) also suggested that phytic acid alone may not fully account for the cooking time since at low phytic acid contents, pectin in the middle lamella forms an insoluble pectate with the cations thereby resulting in poor cookability. In fact, Kumar *et al.* (1978) observed that even though phytic acid decreased with germination of cowpea and chick pea while cooking time correspondingly increased, a similar trend was not noted in germinated green gram. This observation suggests that chemical changes involved in the process of germination may also be implicated in cookability in the case of germinated legumes. Kon and Sanschuck (1981) have, however, reported a better correlation between the ratio of percentage phytic acid/percent calcium present in beans and their cooking times.

The varieties of cowpea investigated here which have shorter cooking times can be considered for selection and development if found to possess good yield and nutrient contents.

ACKNOWLEDGMENT

The author is grateful to the Director of the National Cereal Research Institute, Ibadan, Nigeria for making available the samples and to the University of Ibadan for financing the project through the Senate Research Grants.

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HEAT STABILITY AND SALT BALANCE OF BUFFALO MILK AS AFFECTED BY CONCENTRATION AND ADDITION OF CASEIN

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Received for Publication April 4, 1983
Accepted for Publication July 12, 1983

ABSTRACT

The influence of concentration and addition of 0.5 and 1.0% acid casein on the heat stability (determined as heat coagulation time (HCT) at 130°C) as well as the salt balance of buffalo milk was studied. This was compared to bovine milk. It was observed that buffalo milk was more stable than bovine milk when heated in its fluid state with HCT values of 32.3 min as compared to 31.3 min for cows' milk. However, concentration caused a greater destabilization of buffalo milk (HCT = 2.9 min) as compared to bovine milk (HCT = 6.6 min). The greater decrease in the HCT of buffalo milk may be attributed to a greater disruption of the salt equilibrium and a larger decrease in pH caused during concentration.

Casein addition had a stabilizing effect on the concentrated buffalo milk but not on the fluid milk due to its effect on the salt balance. While calcium, magnesium and phosphate shifted from the dissolved to the colloidal phase the shift in the citrate ion was reverse.

INTRODUCTION

The unstability of buffalo milk to heating for concentration and sterilization poses considerable problem and so far has prevented the manufacturing of evaporated milk from it on a commercial scale (Srinivasan *et al.* 1967). Such a problem encountered during the processing of buffalo milk has been attributed to its lower heat stability (Ganguli 1979). However, some of the studies (Puri and Parkash 1963; Singh and Roy 1978) on the comparison of the heat stability of the two milks revealed that buffalo milk is more stable than bovine milk when heated in its fluid condition. Thus, during concentration the greater destabilization of buffalo as compared to bovine milk is responsible for rendering it unsuitable for the manufacturing of evaporated milk which has to be sterilized. So far no work has been done on this aspect of buffalo milk. Roy and Yadav (1972) reported that it

Journal of Food Processing and Preservation 7 (1983) 151-160. *All Rights Reserved*
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was possible to manufacture evaporated milk from buffalo milk with the addition of acid casein but no work has been done on the influence of this on the heat stability of milk. The present study was undertaken to investigate the influence of concentration and addition of casein on the heat stability of buffalo milk. Five samples of bovine milk were also analyzed to study the influence of concentration on its heat stability for making the comparison of the milk from two species. Further, the influence of concentration and addition of casein on the salt balance (partitioning of four salt constituents, namely, calcium, magnesium, phosphate and citrate and their molar ratios in the dissolved phase) was also determined for an understanding of the mechanism of alteration in the heat stability caused by these factors.

MATERIALS AND METHODS

Milk Samples

Composite milk samples from at least ten Murrah breed buffaloes of the Institute herd were collected during the morning milking in a clean and dry aluminium container. Likewise, composite milk samples from at least ten cross breed (bovine) cows were collected and used for the experiments.

Preparation of Acid Casein and Its Addition to Milk

The acid casein was prepared from buffalo skim milk, following essentially the iso-electric preparation method at pH 4.80 with the addition of 0.5 N-hydrochloric acid (Dunn 1950). The fine precipitate was filtered through muslin cloth. To remove the acid and adhering minerals the casein was washed several times with distilled water and filtered through a Buchner funnel using whatman No. 40 filter. Care was taken to keep the precipitated casein moist up to the time of its addition to milk. The moisture content of this acid casein was determined. From this the necessary quantitites of casein to add to buffalo milk was determined to give the final concentrations (on dry weight basis) of 0.5 and 1.0 g/100 ml milk. After addition the solution was mixed thoroughly by gentle agitation. Both the casein incorporated lots and control were prewarmed (at 85° ± 1°C for 5 min). After cooling to room temperature each lot was divided into two portions. One portion from each lot was concentrated in 1:2 ratio as described below, the other portion was kept as control and used along with concentrated milk for the partitioning of phases through ultracentrifugation and determination of heat stability and pH.

Concentration of Milk

Milk samples (with and without casein incorporation) were concentrated in a rotary vacuum evaporator at 52° ± 1°C (at an absolute pressure of 0.3 mm of mercury) by dipping the flask containing the milk in a water bath maintained at 52° ± 1°C. The concentration was determined gravimetrically.

Separation of Dissolved and Colloidal Phases

Both the fluid and concentrated milk with and without containing added casein were centrifuged at 35,000 rpm (105,000xg) for 50 min at about 20°C in a preparative ultracentrifuge (Beckman Model-L). The serum was drained as completely as possible, collected and used for the determination of dissolved minerals. The proportions of the dissolved minerals in the corresponding milk samples were calculated by compensating for the volume of fat and casein in the milk.

Determination of Heat Stability

Heat stability of all samples of fluid and concentrated milks was determined as heat coagulation time (HCT) at 130° ± 1°C according to the method of Davies and White (1966) as modified by Jairam *et al.* (1976).

Milk samples in duplicate (one ml each) were put in glass tubes (10 cm in length with 0.8 mm internal diameter and corked at both the ends with silicon rubber corks.) These were agitated at 8 cycles per min in an aluminum carriage. To facilitate the observation of protein clotting a lamp was used to illuminate the tubes from above. The HCT (heat clotting time) was recorded as the time elapsed from the moment the tubes were put into the oil bath at 130° ± 1°C to the first appearance of coagulation. The average from the times from two tubes was taken as the HCT value. Time to HCT can be measured to ± 5 s.

Analytical Procedures

Calcium, magnesium, phosphate (as P) and citric acid concentrations were determined as per Sindhu and Roy 1973. In addition fat and protein were measured as before (Sindhu and Roy 1973).

Statistical Analysis of the Data

Statistical analysis of the data by the F test ($p \leq 0.1$) was carried out on a programable minicomputer (HCL-Micro 2200). To study the influence of

concentration on the heat stability and salt balance twenty replicates were analyzed in case of buffalo milk and 5 replicates in the case of cows milk. For the influence of added casein on the heat stability and salt balance of buffalo milk 5 replicates were analyzed.

RESULTS AND DISCUSSION

Results for the heat stability determined as heat coagulation time (HCT) at 130°C and pH of fluid and concentrated buffalo and bovine milk (1:2) are given in Table 1. Similarly the results for the influence of concentration on the total and dissolved proportions of salt constitutents are given in Table 2.

Table 1. HCT (at 130°C) and pH of buffalo fluid and concentrated (1:2) milk[a]

Sr. No.	Parameter	Fluid Milk	Concentrated Milk	Change Due to Concentration
1	HCT (in min.)	32.28 (31.82)	2.89 (6.58)	− 29.39 −(25.24)
2	pH	6.80 (6.66)	6.60 (6.50)	− 0.2 − (0.16)

(a) Results represent the average of 20 composite milk samples.

Values in parenthesis are for the average of HCT and pH of 5 samples of cows' milk analyzed for making the comparison.

It was evident from the results (Table 1) that concentrating buffalo milk to a 1:2 ratio drastically decreased its HCT from 32.3 min to 2.9 min. Statistical analysis of the data revealed that the decrease in the HCT due to concentration was significant ($P \leq 0.1$). Similarly a considerable and significant ($P \lesssim 0.1$) decrease was observed in the dissolved proportions of all the four salt constituents (F values: 17.85 for calcium; 11.46 for magnesium; 40.37 for phosphorus, and 62.75 for citric acid). Further, the decrease was comparatively higher in the dissolved proportions of anions (phosphate and citrate) than cations (calcium and magnesium) which was evident from the increase in the molar ratios of Ca/P and (Ca + Mg) /(P + Cit.) in the dissolved phase. The ratio of Ca/P significantly increased from 1.04 in fluid milk to 1.11 in the 1:2 concentrate. Likewise, the (Ca + Mg)/(P + Cit.) ratio significantly increased from 0.77 to 0.83 due to concentration. However, such an increase in the dissolved proportions of the salt constituents due to concentration was not proportional to the corresponding decrease in the volume of milk (1:2).

Table 2. Partitioning of salt constituents and molar ratios of buffalo fluid and concentrated (1:2) milk[a]

Sr. No.	Constituent	Concentration: Fluid Milk: Total mg/100 ml	Fluid Milk: Dissolved mg/100 ml	Fluid Milk: Dissolved Percent	Concentrated Milk: Total mg/100ml	Concentrated Milk: Dissolved mg/100ml	Concentrated Milk: Dissolved Percent	Change in the Dissolved Phase (%) Due to Concentration
1.	Calcium	194.20	41.94	21.6	388.39	72.88	18.8	−2.8
		(123.52)	(43.54)	(35.2)	(247.04)	(73.52)	(29.8)	(−5.4)
2.	Magnesium	18.62	10.03	53.9	37.24	18.53	49.7	−4.2
		(11.93)	(7.86)	(65.9)	(23.86)	(15.00)	(62.9)	(−3.0)
3.	Phosphorus	95.80	31.70	33.1	191.60	51.50	26.8	−6.3
		(88.90)	(34.22)	(38.5)	(177.80)	(57.38)	(35.0)	(−3.5)
4.	Citric acid	217.97	166.22	76.3	435.94	280.50	64.3	−12.0
		(181.10)	(158.23)	(87.41)	(362.20)	(260.76)	(72.0)	(−15.4)
5.	Ca/p[b]	1.60	1.04		1.60	1.11		+ 0.07
		(1.084)	(0.99)		(1.084)	(0.92)		(−0.07)
6.	(Ca + Mg)/(P + Cit.)	1.35	0.77		1.36	0.83		+0.06
		(0.942)	(0.74)		(0.942)	(0.74)		(nil)

(a) Results represent the average of 20 composite milk samples.

(b) Molar ratios were calculated from the molar concentrations of salts in milk and whey respectively, for total and dissolved phase.

Values in parenthesis are for dissolved proportions of salt constituents and their molar ratios in 5 samples of cows' milk analyzed for comparison.

The present value of HCT of buffalo milk at 130°C, (32.3 min) was within the range of 11.0 to 38.0 min and 8.0 to 49.5 min at the same temperature reported by Abd-El-Salam (1965), respectively for composite and individual milk samples of buffalo milk. Further, the comparison of this value with the HCT value of cows' milk, (31.8 min) determined at the same temperature revealed that buffalo milk was more heat stable at its normal fluid condition. However, due to concentration, the HCT of buffalo milk was drastically decreased from the initial 32.3 min to only 2.9 min. On the other hand, although the initial HCT of fluid cows' milk was slightly less than the same for buffalo milk (Table 1), its HCT after 1:2 concentration was higher (6.6 min).

These findings help to provide an explanation for the instability of buffalo milk during the manufacture of evaporated milk which has to be sterilized after concentration. The reason milk is probably the dramatic disruption of the salt equilibrium which in turn results in a greater decrease in the pH as compared to the cows' milk as also has been noted by Webb *et al.* 1974. Greater disruption in the salt equilibrium in buffalo milk was evident from the greater alteration in its molar ratios and pH caused by concentration. In case of buffalo milk the Ca/P ratio increased from 1.04 in the fluid milk to 1.11 in the concentrated milk while the (Ca + Mg) /(P + Cit.) ratio was increased from 0.77 to 0.83. On the other hand, for cows' milk statistical analysis of the data revealed that these two ratios remained unaltered during concentration indicating a uniform shift of both cations and anions from the dissolved to the colloidal phase. The greater change in the salt equilibrium of buffalo milk also caused a comparatively higher decrease in its pH, 0.2 unit (from 6.8 to 6.6) as compared to only 0.16 unit (from 6.66 to 6.5) in cows' milk. A similar reason (the decrease in pH and the maintenance of high calcium ion concentration during heating rather than the existence of a high initial calcium concentration) was suggested by Evenhuis (1957) for causing the destabilization of milk during concentration.

Results for the effect of the addition of acid casein in buffalo milk at 0.5 and 1.0% level on its HCT and salt balance are shown in Table 3 and Fig. 1. It is evident from the HCT and LSD values in Table 3 and Fig. 1 that addition of casein progressively and significantly decreased the HCT of buffalo milk when heated in its fluid condition. On the other hand, the HCT of concentrated milk was increased due to addition of casein. However, the statistical analysis (F test) of the data disclosed that the increase in the HCT was significant only in concentrate prepared from the milk containing 1.0% added casein. Addition of casein also significantly influenced the partitioning of all the salt constituents except calcium. While magnesium and phosphate shifted from the dissolved to the colloidal phase in both, the fluid milk and its concentrate resulting in a significant de-

Table 3. Influence of added casein on salt constituents (concentrations and molar ratios in dissolved phase) and HCT of buffalo milk and its 1:2 concentrate[a]

Sr. No.	Parameter	Fluid Milk Control	Fluid Milk 0.5% Casein	Fluid Milk 1% Casein	Concentrated Milk Control	Concentrated Milk 0.5% Casein	Concentrated Milk 1% Casein	LSD
1.	Calcium[b]	46.15 (23.7)	43.63 (22.5)	41.75 (21.5)	41.59 (21.4)	40.23 (20.7)	39.58 (20.4)	2.48
2.	Magnesium[b]	9.89 (56.9)	9.02 (51.9)	8.71 (50.1)	9.32 (53.6)	8.96 (51.5)	8.58 (49.3)	0.66
3.	Phosphorus[b]	27.72 (30.7)	27.0 (29.9)	25.74 (28.5)	23.52 (26.0)	22.56 (25.0)	21.84 (24.2)	1.49
4.	Citric acid[b]	168.30 (74.3)	180.93 (79.9)	190.81 (84.3)	142.14 (62.8)	147.51 (65.2)	152.06 (67.2)	5.81
5.	Ca/P	1.30	1.28	1.30	1.38	1.41	1.45	—
6.	(Ca + Mg)/(P + Cit.)	0.88	0.86	0.78	0.94	0.92	0.90	0.067
7.	HCT (in min.)	29.66	27.84	25.55	3.98	5.05	6.75	1.69
8.	pH	6.84	6.80	6.77	6.68	6.64	6.60	0.0612

(a) Results represent the average of 5 samples.

(b) Concentration of salt constituents is in mg/100 ml milk or 50 ml concentrate.

Values in parenthesis are for the percents of salt constieunts in dissolved phase out of total 194.33, 17.39, 90.4 and 226.39 mg of calcium, magnesium, phosphorus and citrate respectively/100ml milk and /50 ml concentrated milk.

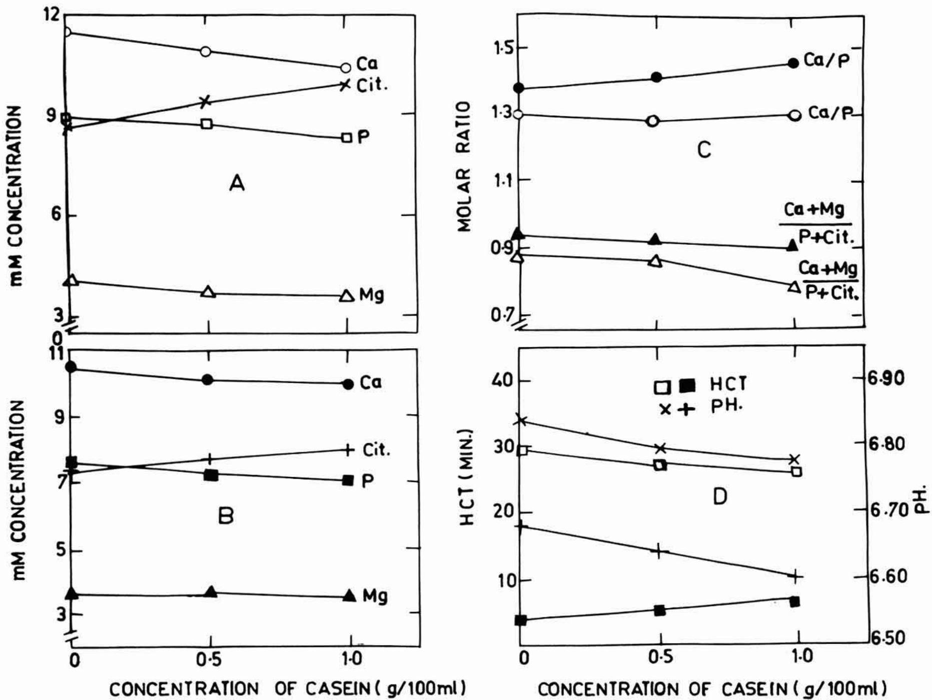

FIG. 1 EFFECT OF ADDED CASEIN ON THE SALT BALANCE, HCT AND pH OF BUFFALO MILK

(A) — Molar concentrations in fluid milk
(B) — Molar concentration in concentrated milk
(C) — Molar ratios
(D) — HCT and pH

○ Δ □ X — fluid milk
● ▲ ■ + — concentrated milk

crease in their dissolved proportions, the shift in the citrate was from the colloidal to the dissolved phase. Due to an increase caused in the dissolved citrate by the addition of casein the (Ca + mg) /(P + Cit.) ratio decreased progressively in the fluid milk. However, in its concentrate the decrease was not significant. On the other hand, casein addition had no significant influence on the Ca/P ratio in fluid milk and its concentrate because both the salt constituents were uniformly decreased.

The present findings, which revealed that the addition of casein to buffalo milk caused a progressive increase in the HCT of concentrated milk were in agreement with the observation of Roy and Yadav (1972) who reported that it was possible to manufacture evaporated milk from buffalo milk with the addition of acid casein but, could not explain why. The

present work suggests the casein incorporation into milk caused a shift in salt constituents from the dissolved to the colloidal phase. Such a decrease in the dissolved and ionic salt-constituents, particularly the decrease in ionic and dissolved calcium and magnesium in the buffalo milk concentrate prepared from the milk containing added casein may be the cause for the increased heat stability as demonstrated by Pyne (1949). He found that the heat stability of milks relate predominantly to differences in the composition of their serum conponents. The "effective calcium ion concentration" was held to bear an inverse relationship to heat stability (Pyne and McHenry 1955). Further, when milk is concentrated there is a shift of minerals from the dissolved to the colloidal phase which causes a decrease in the net negative charge on the casein micelles. The net negative charge on the casein micelle creates an electrostatic repulsion between the micelles, causing them to remain in solution (Horne 1958). The binding of positively charged Ca^{2+} and Mg^{2+} to the casein micelle reduces its negative charge and hence the repulsion until a critical level is reached at which precipitation occurs. The addition of casein to milk will impart greater stability to the casein micelle during concentration of milk because to neutralize the charge on the casein micelle to the level of precipitation, a greater calcium concentration will be required. The requirement of a higher calcium level to neutralize the negative charge on the casein micelle will cause a delay in the coagulation of concentrate which means a greater stability of the concentrate.

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KINETICS OF OXIDATION OF DEHYDRATED FOOD AT LOW OXYGEN PRESSURES

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Received for Publication August 3, 1983
Accepted for Publication August 24, 1983

ABSTRACT

Kinetic studies were performed to obtain the dependence of rates of lipid oxidation on oxygen pressure, in a system containing free as well as adsorbed oxygen. The model system consisted of methyl linoleate dispersed on either microcrystalline cellulose or on nonfat milk powder. Oxidations were carried out at 37°C, and with headspace concentrations of oxygen ranging from 0.52% to 10.7%. These concentrations were maintained approximately constant by periodically resupplying oxygen to replace the amount reacted with the lipid.

Bimolecular oxidation kinetics were found in both systems with the rate of oxidation more rapid (by a factor of 5 to 6) in the cellulose system. The dependence of oxidation on oxygen pressure was of a form previously found for oxidizing lipids by other investigators, and is consistent with theoretical considerations. The slower oxidation in the milk system appeared to be due to two factors: encapsulation of part of the lipid in the milk solids, and the lower internal surface area of the milk solids compared to the cellulose support.

Journal of Food Processing and Preservation 7 (1983) 161-178. *All Rights Reserved*
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INTRODUCTION

Lipid oxidation is a major cause of quality deterioration in dehydrated foods. A common method of controlling the oxidation reaction is to reduce the 0_2 concentration in the headspace over the food by vacuum or nitrogen packing. The O_2 concentration is never reduced to zero by these methods, however, and oxidative damage can still occur in sensitive foods.

Among studies on oxygen-dependence of oxidation were those performed on pure fatty acids by Henderson and Young (1942), Bolland (1949), Bateman (1954), Karel (1960), and Marcuse and Fredriksson (1968, 1969). Karel (1960) and Marcuse (1967) also studied oxygen dependence of oxidizing lipids in model systems. Food systems were studied by Tuomy *et al.* (1968a; 1968b; 1969; 1970); Bishov *et al.* (1971); Marcuse (1967); Quast and Karel (1971; 1972a; 1972b), and Simon *et al.* (1971). The oxygen dependence of rates of oxidation has often been described by Eq. (1):

$$\text{Rate} = [0_2]/(B_1 + B_2[0_2]) \quad (1)$$

where: $[0_2]$ is oxygen concentration
B_1 and B_2 are constants.

In the present work we studied the effect of low concentrations of headspace oxygen on the rate of reaction of methyl linoleate dispersed on microcrystalline cellulose and on nonfat dry milk.

MATERIALS AND METHODS

Headspace Gas Measurement

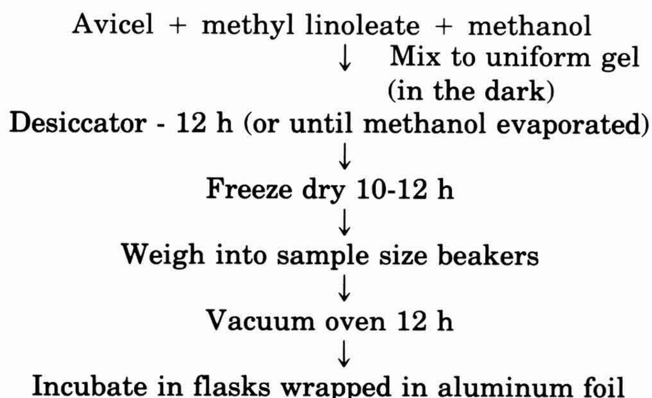
A teflon-membrane-covered oxygen electrode (Model 777, Beckman Instruments, Fullerton, CA) was used for these measurements. It was connected to one end of a calibrated 2 ml pipette whose other end was joined to a 3-way stopcock. The probe was calibrated for operation at oxygen pressure higher than 5% by adjusting the zero setting when the system was evacuated, and the full scale setting at 21% oxygen when exposed to air. For 0_2 readings of less than 5% 0_2, full scale was set to 5% by calibrating against a manometrically determined oxygen pressure corresponding to a low concentration of oxygen at standard atmospheric conditions (Teixeira-Neto *et al.* 1981).

When a headspace measurement was desired, the sample flask (closed via a hose clamp) was connected to the free arm of the 3-way stopcock and a vacuum pulled on the system. Once the previously calibrated probe showed a steady zero reading, the stopcock was turned so as to engage only the evacuated pipette (with the 0_2 probe at one end) and the sample flask.

The hose clamp was removed from the sample flask and the headspace gas in the flask filled the pipette. The 0_2 partial pressure was measured with the 0_2 probe. Since the total pressure, volume, and temperature were known, the ideal gas equation was used to derive the molar concentration of oxygen in the headspace of the flask.

Preparation of the Samples

The model system consisted of Avicel microcrystalline cellulose PH 101 (FMC Corp., Philadelphia, PA) and methyl linoleate (Nu Chek Prep, Elysian, MN). The preparation procedure was as follows:



The milk-lipid system consisted of nonfat dry milk (Carnation Co., Los Angeles, CA) and methyl linoleate (Nu Chek Prep, Elysian, MN) prepared identically to the model system except that after freeze drying, the powder was granulated in a coffee mill for a more uniform consistency. Initial lipid concentration was 0.1 g lipid/g dry powder. All samples were stored at 37°C.

Filling the Flasks with Various $0_2/N_2$ Mixtures

The sample flasks to be incubated were initially adjusted to the desired gas composition in the following manner: A manifold was constructed with ports to 10 sample flasks, a port leading to a manometer and a 3-way stopcock with one arm connected to the manifold, one arm to a vacuum pump, and the other arm to the compressed tanks of $0_2/N_2$ mixtures (Matheson Gas Co., Gloucester, MA).

The flasks were evacuated and then filled with the desired gas mixture. This process was repeated several times to allow equilibration of the sample with the desired gas composition.

Diene Conjugation Analysis

This method involved the extraction of 0.5 g of the model system with 50 ml of methanol with the subsequent determination of U.V. absorbance at 233 nm in a Hitachi-Perkin Elmer 200 spectrophotometer. The extinction coefficient of conjugated dienes is 29000 (Privett and Blank 1962) compared to 6026 (CRC Atlas of Spectra Data and Physical Constants, Vol. III) for nonconjugated methyl linoleate. The assumption on which this test is based is that the major oxidation products are conjugated hydroperoxides.

Sorption Isotherms

The sorption isotherm of dried milk was prepared by weighing one to two gram samples (containing no added lipid) into petri dishes. The petri dishes were placed in desiccators containing saturated salt solutions with water activities ranging from 0.065 (KOH) to 0.539 (NaBr) at 37°C. These samples were repeatedly weighed until they reached equilibrium, at which time (up to 76 days) the moisture content on a dry basis was calculated.

RESULTS AND DISCUSSION

Model System Studies

Correlation of Oxygen Uptake Values with Diene Conjugation. Oxygen uptake as measured by the oxygen probe was compared with diene conjugation. Assuming that in the initial stages of the reaction the major oxidation products are conjugated hydroperoxides with an extinction coefficient of 29000, one can follow the build up of the conjugated hydroperoxides spectrophotometrically at 233 nm (Privett and Blank 1962). Also, assuming a one to one stoichiometry between peroxide formed and 0_2 absorbed, the reacted oxygen is easily calculated. The value of the correlation lies in being able to assess whether all oxygen disappearing from the headspace has in fact reacted with the lipids of the model system.

Figure 1 shows the oxidation of the model system at 0.52%, 1.05%, and 2.17% 0_2. The oxygen uptake followed typical bimolecular oxidation kinetics, and could be readily correlated by Eq. (2), derived previously by Maloney *et al.* (1966),

$$\frac{dy}{dt} = K_B (y) (1-y) \quad (2)$$

where y = oxygen absorbed (moles/mole linoleate)
t = time
K_B = overall constant for the particular system.

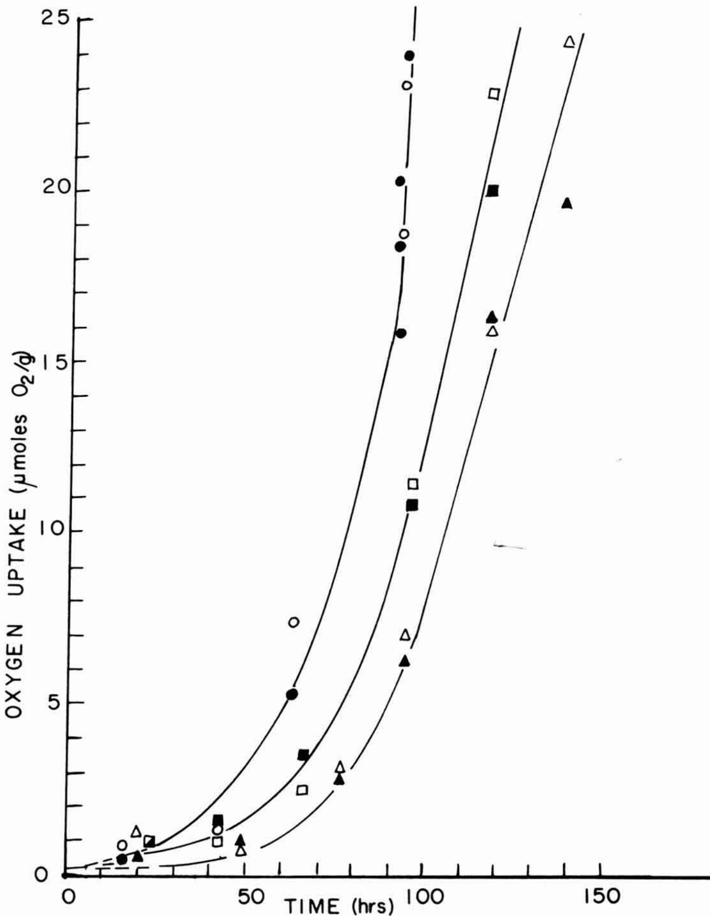


FIG. 1. OXIDATION OF THE CELLULOSE MODEL SYSTEM AT 0.52%, 1.05% AND 2.17% OXYGEN
Solid circles, diene conjugation, 0.52% O_2
Open circles, oxygen uptake, 0.52% O_2
Solid squares, diene conjugation, 1.05% O_2
Open squares, oxygen uptake, 1.05% O_2
Solid triangles, diene conjugation, 2.17% O_2
Open triangles, oxygen uptake, 2.17% O_2

Because the amount of substrate depletion due to oxidation could be ignored the quantity (1-y) could be considered equal to 1.0, and the simplified equation integrated to give:

$$y = y_o e^{K_B t} \quad (3)$$

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The equation could be readily transformed to relate oxygen absorption per unit weight of sample to time.

$$0_2 \text{ uptake } (\mu \text{ mole/g}) = B \exp(Kt) \qquad (4)$$

where K = bimolecular constant (h^{-1})
t = time in hours
B = constant

The curves were calculated using a calculator program which linearized the data by taking the natural logarithm of the 0_2 uptake values and performed a linear regression on the transformed data. The slope of the line is equal to the 1st order bimolecular rate constant. The quality of the fit is determined via the coefficient of determination (r^2).

Figure 1 shows that the agreement between the two methods is quite good. In order to quantitatively determine how well the two methods compared, oxygen absorption was plotted against the data determined by diene conjugation at each sampling time and the correlation coefficient (r^2) determined. The results of this analysis are shown in Table 1 for the different runs at the four oxygen concentrations. It can be seen that the agreement between the two methods is excellent. Thus, the method of 0_2 uptake measurement using an oxygen probe at low concentrations of oxygen correlated very well with a chemical method, measuring a major oxidation product.

Kinetic Studies

In order to avoid variations due to differences in the method of preparation, oxygen pressure dependence of oxidation was studied in a run using the same batch of model system at O_2 concentrations of 0.52%, 1.05%,

Table 1. Correlation coefficients between O_2 uptake and diene conjugation

0_2 Concentration (%)	Correlation Coefficient (r^2)
0.52	.996
	.996
1.05	.974
	.974
2.17	.994
	.994
5.49	.992

2.17%, and 5.49%. This data is plotted in Fig. 2 on semi-log coordinates. A linear relation was obtained (Fig. 3) between the reciprocals of oxygen

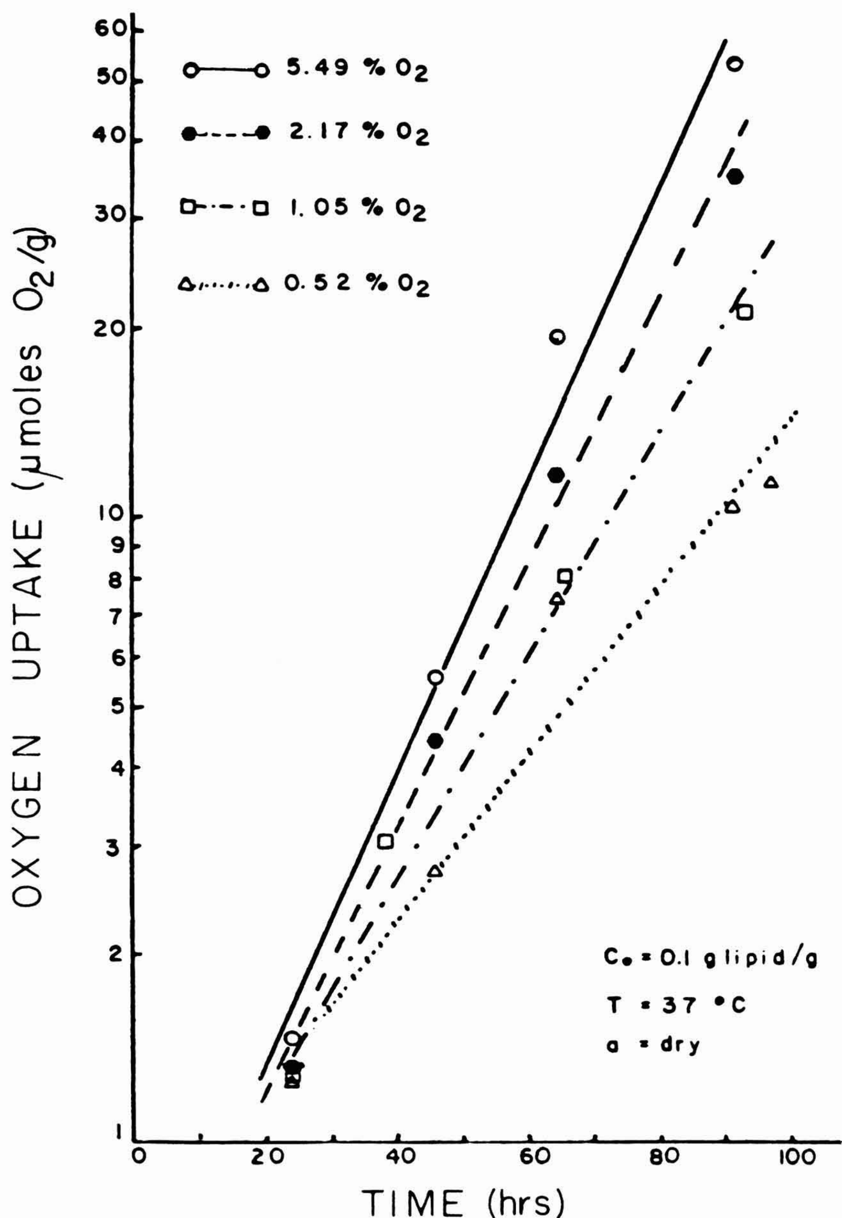

FIG. 2. FIRST ORDER PLOT FOR OXIDATION OF THE CELLULOSE MODEL SYSTEM AT SEVERAL OXYGEN CONCENTRATIONS (r^2 values were: 0.957 at 5.49% O_2, 0.985 at 2.17% O_2, 0.988 at 1.05% O_2 and 0.983 at 0.52% O_2).

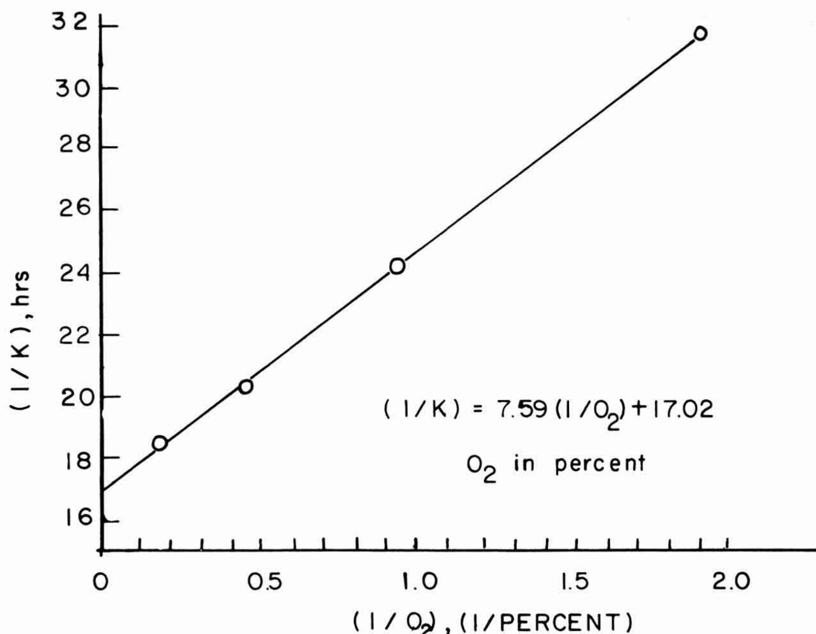

FIG. 3. A PLOT OF (1/K) VERSUS $1/[O_2]$ FOR THE CELLULOSE MODEL SYSTEM (C_o = 0.1 g lipid/g; T = 37°C, dry)

concentration and of K (derived from Fig. 2). A least squares analysis yields the following equation,

$$\frac{1}{K} = 7.59 \frac{1}{[O_2]} + 17.02 \tag{5}$$

with a correlation coefficient (r^2) = .999. Inverting the above equation to get the direct relation of K to $[O_2]$,

$$K = \frac{[O_2]}{7.59 + 17.02\,[O_2]} \tag{6}$$

This equation is plotted in Fig. 4 where the effect of oxygen concentration on rate is directly seen. Using Eq. 6 and extrapolating above oxygen concentrations of about 10%, there is essentially no effect of oxygen concentration on K, whereas between O_2 concentrations of about 3% to 10% there is a very slight effect. Below O_2 concentrations of 2%, however, the effect on rate is dramatic with the rate decreasing sharply as the O_2 is decreased.

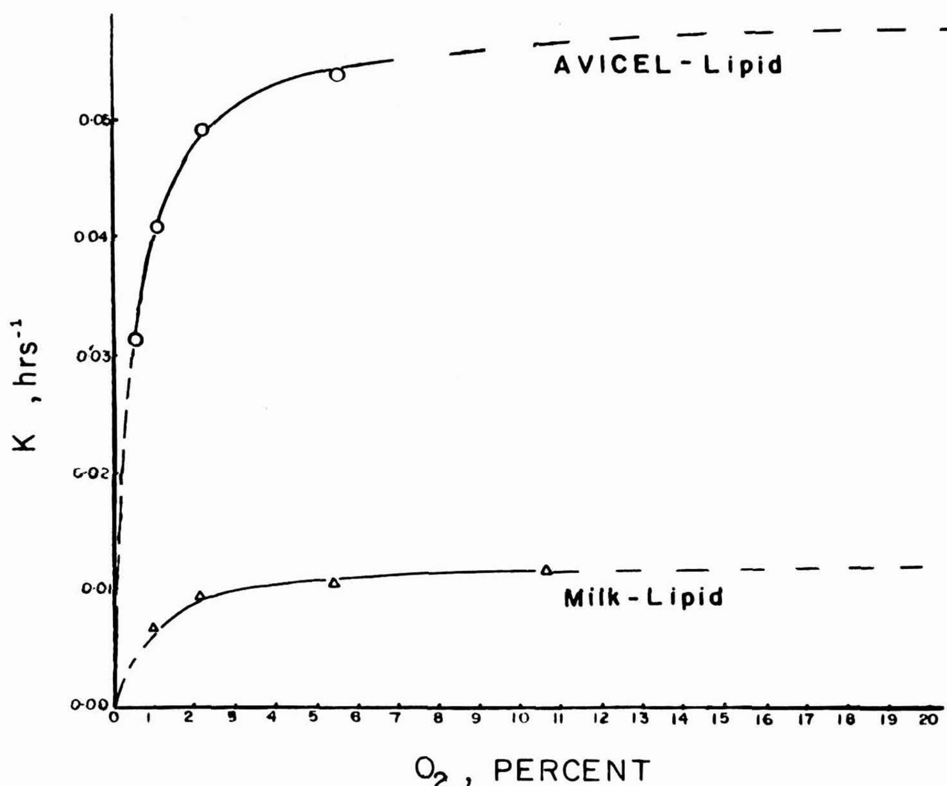

FIG. 4. OXYGEN DEPENDENCE OF THE CELLULOSE SYSTEM AND OF THE MILK SYSTEM (C_o = 0.1 g lipid/g, 37°C, dry)

Milk System Kinetic Studies

In order to study the oxidation rate dependence on oxygen concentration in a food system, nonfat dry milk was mixed with methyl linoleate as described in the Materials and Methods section. This method of dispersion was chosen because the cellulose model system had been prepared in the same way, thus allowing a more meaningful comparison of the results.

Figure 5 shows the oxidation of methyl linoleate on nonfat dry milk powder in a typical run. The kinetic analysis showed behavior similar to that in the cellulose system, and the results were analyzed using Eq. (3). The results are tabulated in Table 2 where the coefficient of determination shows the closeness of fit to a first order model.

Overall, it can be seen from Table 2 that the data fit quite well at all oxygen concentrations except for the first run at 1.05% O_2 where r^2 = 0.761. In the second run, the reaction was carried out to higher oxidation

Table 2. Rate constants and O_2 concentrations for the milk-lipid system

$[O_2]$	K (h^{-1})		r^2		$1/[O_2]$	1/K (h)		K_{avg}**
(%)	(1)*	(2)*	(1)	(2)	(1/%)	(1)	(2)	(h^{-1})
1.05	.0071	.0062	.761	.976	.95	140.85	161.29	.0067
2.17	.0087	.0103	.947	.977	.46	114.94	97.09	.0095
5.49	.0113	.0101	.949	.973	.18	88.50	99.01	.0107
10.69	.0105	.0133	.926	.894	.094	95.24	75.19	.0119

*Denotes different runs
** $K_{avg} = [K(1) + K(2)]/2$

levels at 1.05% O_2 and the exponential character of the data became more apparent ($r^2 = 0.976$ for this run) although the rate constant is lower than for the 1st run.

Table 2 also gives the values of 1/K and $1/[O_2]$ required for the linear regression. The least squares analysis of the data gave the following expression,

$$1/K = 77.30 + 75.11\,(1/[O_2]) \quad (7)$$

$$r^2 = 0.876$$

There was some scatter of the data, probably due to slight differences in preparation of the batches and variations of the milk itself. Inverting this equation to get a more direct representation of K = f (% O_2) yields,

$$K = \frac{[O_2]}{75.11 + 77.30\,[O_2]} \quad (8)$$

and a plot of the oxygen dependence in this form is shown in Fig. 4. In this figure, the average values of K (last column in Table 2) for the two runs are plotted on the curve which is shown extending by extrapolation down to 0% O_2 and out to 21% O_2. From the curve one can observe that above 9-10% O_2 there is essentially no change in rate with change in O_2 pressure. A slight decrease in rate is demonstrated between 5-9% O_2 and below this, the rate-decreasing effect of lowering of the O_2 concentration becomes increasingly pronounced.

Comparison of Model System and Milk System Results

Figure 4 shows also a comparison of the oxygen dependence of rate for the two systems studied.

While the general shape of the two curves is similar and the equations fit the data quite well, the rate of oxidation of the two systems is different. The rate constants for the Avicel-lipid system are 5 to 6 times greater than the corresponding constants for the milk-lipid system. The experimental

rate constants are displayed in Table 3 along with rate constants for similar systems from the literature.

One would expect that the rate of oxidation of the oil in the milk powder would be lower than the rate on cellulose since the milk contains protein which could interact with the lipid, thus preventing mobility of the fatty acid chains or directly inhibiting free radical propagation (Karel 1977).

The rate in the milk system could also be lower due to encapsulation of the lipids in an amorphous lactose-protein matrix preventing O_2 from reaching any lipid not on the surface except by very slow O_2 diffusion. A third possibility is that the surface areas of the two systems were sufficiently different to affect the rate of oxygen uptake. These latter two physical rate-inhibitory possibilities were tested as described below.

Encapsulation Effects

In order to test the possibility that part of the lipid was hidden from O_2

Table 3. Comparison between bimolecular rate constants reported in the literature and those observed experimentally

System	$[O_2]$ (%)	T °C	a	K_B (h^{-1})	Ref.
Bulk Methyl Linoleate	21	40	—	6.4×10^{-2}	Kern & Dulog 1959a
Bulk Methyl Linoleate	21	37	—	6.6×10^{-2}	Labuza *et al* 1969
Bulk Ethyl Linoleate	21	40	—	3×10^{-2}	Bateman 1954
Methyl Linoleate in Emulsion	21	40	—	8.5×10^{-2}	Mabrouk & Dugan 1961
Methyl Linoleate Cellulose Powder	21	37	dry	8.2×10^{-2}	Labuza *et al.* 1969
	21	37	.32	5.3×10^{-2}	
	21	37	.50	5.0×10^{-2}	
Methyl Linoleate Filter Paper	21	37	dry	4.6×10^{-2}	Labuza *et al.* 1969
	21	37	.98	6.8×10^{-2}	
Methyl Linoleate Avicel Cellulose	5.49	37	dry	5.39×10^{-2}	Present Study
	2.17	37	dry	4.92×10^{-2}	
	1.05	37	dry	4.12×10^{-2}	
	0.52	37	dry	3.16×10^{-2}	
Methyl Linoleate Nonfat Dry Milk Powder	10.69	37	.55	1.99×10^{-2}	Present Study
	10.69	37	dry	1.19×10^{-2}	
	5.49	37	dry	1.07×10^{-2}	
	2.17	37	dry	0.95×10^{-2}	
	1.05	37	dry	0.67×10^{-2}	

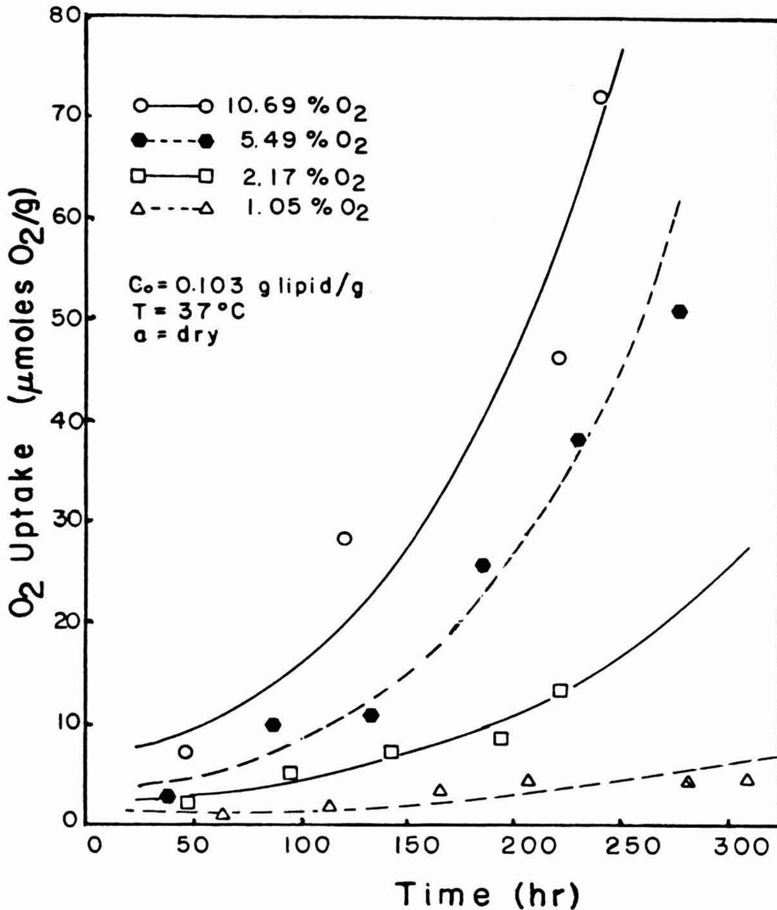

FIG. 5. OXIDATION OF THE MILK SYSTEM AT SEVERAL OXYGEN CONCENTRATIONS

and therefore not able to react, an oxidation run was done at 10.69% O_2 with a humidified sample water activity (a) equal to 0.55 and compared to the rate at these conditions in a dry system. It was shown previously by Gejl-Hansen and Flink (1977), that disruption of the matrix of a dry food by exposure to high water activities exposes encapsulated lipids to oxygen. For the specific case of nonfat milk solids, Saltmarch and Labuza (1980) showed for whey powder, that when the (a) increases above 0.4, lactose begins to crystallize out and "squeezes" out any material entrapped within the matrix. Any entrapped lipids are thus exposed to the oxygen environment. If on the other hand, lipid was not entrapped, increasing (a) to 0.55 would decrease the rate, since water has an antioxidant effect on autoxidation of linoleate (Maloney *et al.* 1966).

Figure 6 shows the results of this experiment. The samples held at the

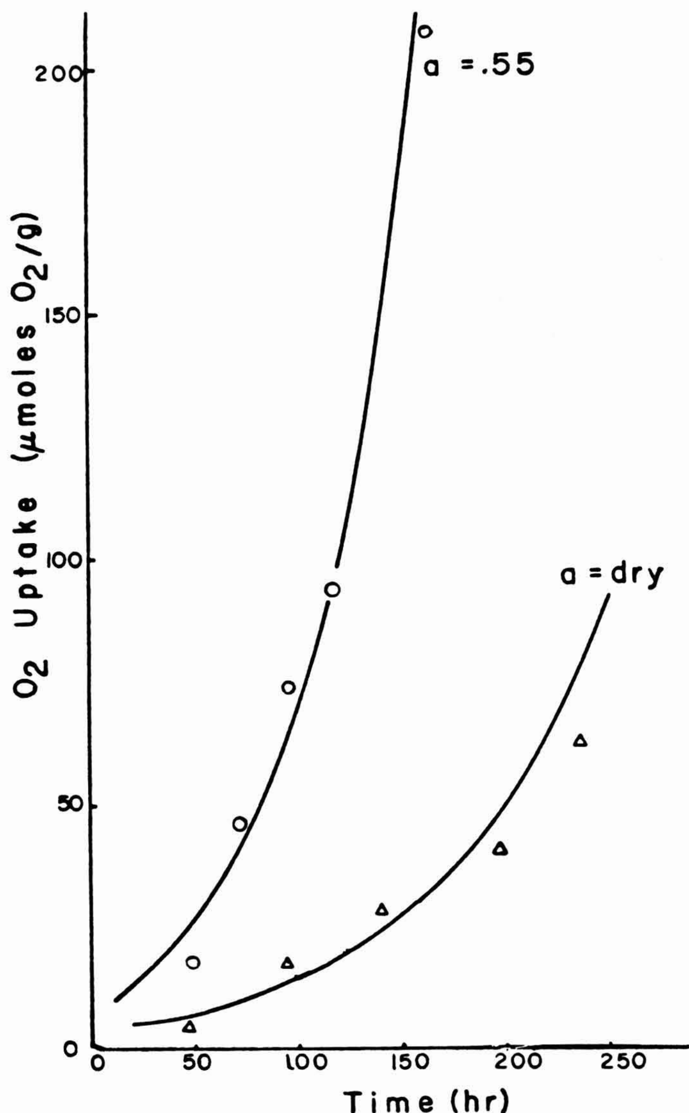

FIG. 6. COMPARISON OF OXIDATION OF THE MILK SYSTEM IN THE DRY STATE AND AT a = 0.55

higher relative humidity oxidized significantly faster than the dry samples. The experimental rate constants for the dry and humid systems were 1.19×10^{-2} and $1.99 \times 10^{-2}\ h^{-1}$, respectively. It would thus appear that encapsulation of lipid was occurring in the milk system and this was responsible in part for the lower observed rates.

It should be noted that this humidification procedure did not necessarily

release all the encapsulated lipid. Also, even if encapsulation was the sole inhibitory mechanism operating in the milk system, this experiment would not show it. If all the linoleate was released by humidification, the rates would probably still be lower than in the dry model system due to water activity effects on oxidation rate.

Surface Area Effects

In order to determine the surface area of the milk system, a B.E.T. isotherm was calculated using the nonfat dry milk prepared as before, but without added lipid and the surface area determined from the monolayer value. The procedure below is the standard one described by Labuza (1968). The B.E.T. equation can be written as, ($a < 0.5$),

$$\frac{a}{(1-a)V} = \frac{1}{V_m B} + \frac{a(B-1)}{V_m B} \qquad (9)$$

where: a = water activity
V = moisture content (g H_2O/g powder)
V_m = monolayer value (g H_2O/g powder)
B = constant

Data given in Table 4 was used to plot the isotherm (Fig. 7). The calculated V_m value was 0.021 g H_2O/g powder.

Table 4. Isotherm data for determination of B.E.T. parameters

a	m (g H_20/100 g powder)	V (g H_2O/g powder)	$\frac{a}{(1-a)V}$ $(\frac{\text{g powder}}{\text{g } H_2O})$
.065	1.09	.0109	6.38
.066	1.29	.0129	5.47
.112	1.57	.0157	8.05
.236	2.38	.0238	13.01
.318	2.60	.0260	17.55
.492	3.94	.0394	24.55
.539	5.14	—	—

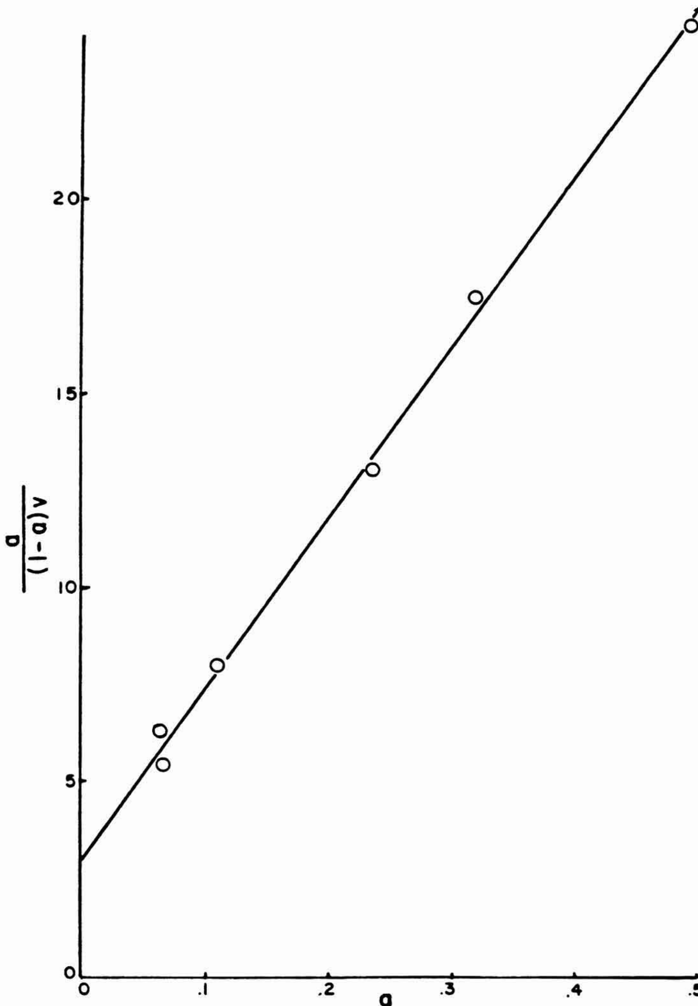

FIG. 7. B.E.T. ISOTHERM PLOT FOR NONFAT DRY MILK

Calculation of Surface Area of Milk Powder

The surface area is given by,

$$S = V_m \times MW_{H_2O}^{-1} \times N_{av} \times H_2O_s \tag{10}$$

where:
V_m = monolayer value (g H_2O/g powder)
MW_{H_2O} = molecular weight of H_2O (g/mole)
N_{av} = Avogadro's number (molecules/mole)
H_2O_s = surface area of H_2O (m^2/molecule)

$$S = (.021) \times (18^{-1}) \times (6.02 \times 10^{23}) \times (10.6 \times 10^{-20}) \simeq 74 \text{ m}^2\text{/gram of milk.}$$

The surface area of the Avicel PH 101 used in the experiment was 138 m^2/g (private communication, FMC Corporation). Bluestein and Labuza (1972) found similar values for Avicel (114 m^2/g).

Since the oxidation studies were performed under dry conditions, it is useful to know whether the B.E.T. surface area thus calculated corresponded to the area before or after the state of lactose in the system had changed.

As previously stated, Saltmarch and Labuza (1980) found that only above $a_w = 0.4$ did the lactose begin to crystallize. If the last point in the B.E.T. isotherm (corresponding to $a > 0.4$) is neglected and the linear regression done only on those points below $a = 0.4$, the resulting monolayer value is still the same as previously found and thus giving the same surface area noted above. The B.E.T. isotherm therefore gives the water surface area in the system of interest, namely the dry milk powder as it was before collapse.

It might therefore be expected that some lowering of the milk system rate constants results merely from the lower surface area of the milk powder compared with the cellulose.

In summary, *both* encapsulation effects and surface area effects decreased the rate of reaction of the milk system. Some lipid-protein effects were probably also operative, however, these were not tested for.

ACKNOWLEDGMENTS

This work was supported in part by grant number I-159-79 from the United States-Israel Binational Agricultural Research and Development Fund (BARD), and by grant CPE-8104582 from the Division of Engineering, National Science Foundation.

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THE INFLUENCE OF GAMMA-IRRADIATION ON THE STORAGE LIFE OF "RED" VARIETY GARLIC

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Received for Publication May 19, 1983
Accepted for Publication September 7, 1983

ABSTRACT

Garlic bulbs from local cultivars were irradiated 30 days after harvest with a dose of 0.03 kGy of Co – 60 gamma rays. A pilot scale sample was stored 300 days in commercial warehouse (6-32°C; 58-86 R.H.). At the end of the storage period the irradiated garlic bulbs had lost 24% of their original weight. After 270 days of storage 79.0 ± 8.4% of the irradiated bulbs were adjudged marketable. The process did not adversely affect the acceptability of the product.

INTRODUCTION

Of the various applications of ionizing radiation in the preservation of horticultural products, shelf-life extension of bulbs and tubers by inhibition of sprouting shows promise. This application is referred to as "radioinhibition". Various investigators (Mathur 1963; Kahan and Padova 1966; El-Oksh *et al.* 1971; Khan and Wahid 1978; Fernández and Arranz 1979), have shown that the process efficacy on garlic bulbs depends upon three essential parameters: physiological state of the bulbs at irradiation time, irradiation process and storage conditions.

In our preliminary studies with "Red" variety garlic, the one most cultivated in this region, a dose of 0.03 kGy of Co – 60 gamma rays given 30 days after harvest was sufficient for sprouting inhibition during storage under laboratory conditions (Curzio *et al.* 1982).

The present paper deals with the results of an investigation in which a pilot scale sample of "Red" variety garlic was irradiated 30 days after harvest and stored in a commerical warehouse (6-32°C; 58-86% R.H.). Weight loss and general quality of marketable bulbs were monitored during storage.

Journal of Food Processing and Preservation 7 (1983) 179-183. *All Rights Reserved*
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MATERIAL AND METHODS

"Red" variety garlic (600kg) grown in the S.E. of the Buenos Aires province and cured naturally in the field for about ten days was used in these studies. About 300 kg of sound and uniformly-sized bulbs were packed in cartons 28 x 30 x 35 cm and irradiated 30 days after harvest at the facilities of Comisión Nacional de Energía Atómica. The samples were treated with a dose of 0.03 kGy at Co -60 gamma rays at the rate of 0.41 Gy/s and a dose uniformity ratio of 1.25.

After treatment, the irradiated and control bulbs were stored in a commerical warehouse for 300 days at temperatures ranging from 6°C to 32°C (R.H. 58-86%).

The following data were recorded monthly: (1) The cumulative percentage mean weight loss on 20 samples of 1,000 $\pm$ 100 g packaged in perforated paper bags was determined by weighing each sample on a Bosch P 115 monoplate balance starting 90 days after harvest. (2) Starting 120 days after harvest the percentage of marketable bulbs was determined on samples of 180 bulbs which were kept on plastic trays. Bulbs that showed external sprouting, rotting or softening were discarded and the remainder were designated as marketable bulbs. (3) Inner sprouting and radiation-induced darkening in the growth center were checked on cloves of marketable bulbs. The criterion adopted for inner sprouting was the presence of a green coloration.

Bimonthly, 50 bulbs were taken at random from 300 kg of piled-out garlic and the percentage of marketable bulbs was recorded.

After about 300 days of storage, sensory evaluation was carried out by a ten-judge taste panel which was asked to rate the acceptability of raw garlic for human consumption.

RESULTS

Nonirradiated garlic bulbs underwent greater physiological losses in weight over 300 days of storage than irradiated ones (Fig. 1). At the end of the storage period the weight losses were 55.0 and 24.0% of the original weight in the nonirradiated and irradiated garlic bulbs, respectively.

Table 1 shows that the percentage of marketable garlic bulbs stored on plastic trays was greater for the irradiated than for nonirradiated ones and began to become even greater after 210 days of storage. Nonirradiated bulbs were discarded due to sprouting and rotting; irradiated bulbs were discarded only due to rotting. Comparable results were obtained on the piled-out garlic bulbs.

FIGURE 1

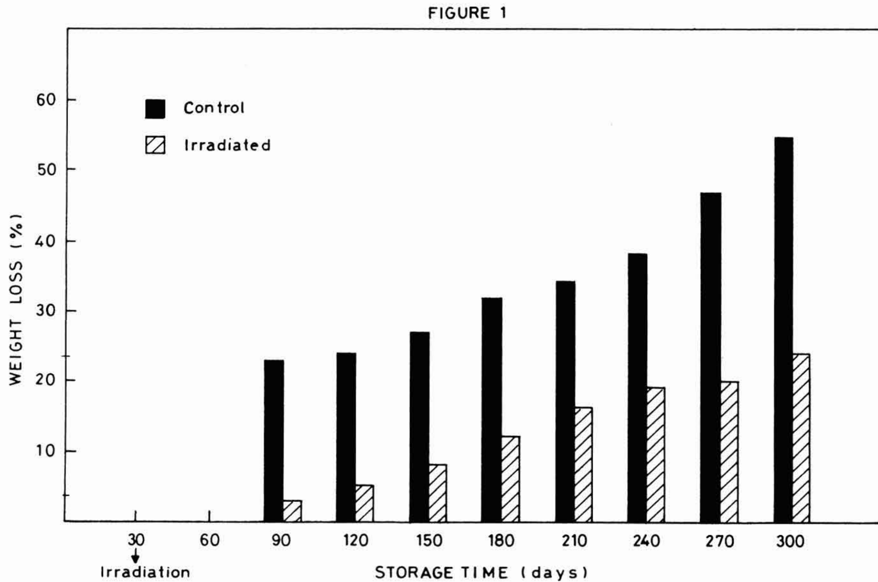

FIG. 1. LOSS OF WEIGHT IN GARLIC BULBS STORED AT 6 -32°C (R.H. 58-86%) UP TO 300 DAYS

Inner sprouting was absent in the cloves of marketable irradiated garlic bulbs throughout storage period, whereas it was already present in 50% of the nonirradiated ones at the start of the testing period (120 days after harvest). Radiation-induced darkening (small spots) in the growth center was evident in 25% and 100% of the cloves after about 150 days and 300 days of storage, respectively.

Sensory evaluation revealed no adverse effects on the organoleptical properties of irradiated garlic at the end of the storage period.

DISCUSSION

Our observations that less weight was lost in irradiated garlic bulbs than in the control are in line with the findings of Mathur (1963); El-Oksh (1971) and Fernández and Arranz (1979). These results may have been due partially to the radiation effects on the biochemical mechanisms involved in the respiration, transpiration and sprouting of the bulbs.

Irradiation increased the percentage of marketable garlic bulbs by suppressing external sprouting since rotting was present in both. Similar results were found by Mathur (1963); Kahan and Padova (1966); El-Oksh

Table 1. Percentage of marketable garlic bulbs stored at 6-32°C (R.H. 58-86%) up to 300 days

Treatment	Percentage of Marketable Bulbs After (Days)						
	120	150	180	210	240	270	300
Control	86.7 ± 5.1	87.0 ± 3.9	72.7 ± 12.3	66.0 ± 13.4	62.4 ± 7.0	35.0 ± 5.8	6.3 ± 2.1
Irradiated	95.5 ± 1.9	93.2 ± 6.1	80.3 ± 11.5	85.0 ± 6.8	86.2 ± 4.1	79.0 ± 8.4	39.6 ± 2.7

(1971); Khan and Wahid (1978) and Fernández and Arranz (1979), under different experimental conditions.

From the taste panel results it can be concluded that the radiation process did not adversely influence the marketability of raw garlic. Thus the browning of the growth center had no influence on the acceptability of the product.

These pilot scale experiments have shown that the radioinhibition process can extend the storage life and decrease weight loss and quality deterioration of locally grown "Red" variety garlic stored under commercial warehouse conditions (6-32°C; 58-86% R.H.).

ACKNOWLEDGMENTS

This work was part of a co-ordinated program of research under the sponsorship of IAEA (Research Agreement n°2615/CF). Thanks are due to the Comisión Nacional de Energía Atómica for carrying out the process. This work was supported, in part, by Comisión de Investigaciones Científicas de la Provincia de Buenos Aires and Subsecretaría de Ciencia y Tecnología de la Nación.

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PHYTATE, PHOSPHORUS AND CALCIUM CONTENTS OF MATURE SEEDS OF *VICIA FABA* L. AND THEIR RELATION TO TEXTURE OF PRESSURE — COOKED FABA BEANS

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Received for Publication June 30, 1983
Accepted for Publication October 25, 1983

ABSTRACT

Twenty samples of faba beans which showed wide variations in the texture after cooking, were analyzed for phytic acid, phosphorus fractions and calcium contents of decoated seeds and seed coats. Wide variations were found in phytic acid, phosphorus and calcium contents among the samples of the same variety and from one year to another. Phytic acid and total phosphorus were concentrated in the decoated seeds while calcium was concentrated in the seed coats. Inorganic phosphorus represented a very small fraction (2 to 4%) of the total phosphorus. However, the mean value of phytate phosphorus constituted about 30% and 40% of the total phosphorus of decoated seeds and seed coats, respectively. A highly significant correlation was found between the total phosphorus and phytate phosphorus contents of decoated seeds. A positive significant correlation between phytic acid content and texture of cooked beans was found for samples of the 1980 crop, but not for samples of the 1981 crop. No significant correlation was found between the phytic acid/Ca ratio and the texture of cooked faba beans. These results indicate that phytic acid content does not affect the texture of cooked faba beans directly, but rather through interrelationships with other seed constituents.

INTRODUCTION

Dry faba beans, like other legumes, vary in their cooking quality or capacity to undergo proper softening when cooked due to differences in seed size and weight, percentage of seed coat, hydration and swelling coefficients, color and percentage of germination (Shehata 1982). Effect

Journal of Food Processing and Preservation 7 (1983) 185-192. *All Rights Reserved*
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of environment on the cooking quality of peas has been reported by Halstead and Gfeller (1964). Mattson *et al.* (1950) postulated that the higher the phytate content in peas, the faster they cook and that at a given phytate concentration, the higher the ratio of monovalent (K and Na) to divalent cations (Ca and Mg), the better is the cooking quality. Halstead and Gfeller (1964) found that the cooking time of field peas was related to phytate and calcium content in a pot experiment but not in a field experiment. Rosenbaum and Baker (1969) reported that the peripheral region of peas' cotyledons cooked less readily than the interior part although the former had the higher phytate content. Muller (1967) suggested that thermal softening of peas and beans was affected mainly by their concentrations of phytic acid, Ca, Mg and free pectin. However, he did not exclude the possibility of other factors such as seed coat thickness and composition. Lolas and Markakis (1975) found a highly significant positive correlation between the total phosphorus and phytic acid contents of beans. They also concluded that almost all of the total phytic acid (99.5%) in beans was water soluble. No direct relationship was found between the phytic acid content of lentils and their cooking time (Wassimi *et al.* 1978). Although large variations were found in phytate content among faba bean samples, highly significant correlation coefficients were found between total and phytate phosphorus contents (Griffiths and Thomas 1981). This is a study on the distribution of phytic acid, phosphorus fractions and calcium between the decoated seed and seed coat and their relationship to the texture of pressure cooked faba beans.

MATERIALS AND METHODS

About 40 samples (20 kg each) were collected directly from different farms (located in the Nile Delta and Middle Egypt) immediately after harvesting in May 1980 and May 1981. The texture of the cooked faba bean samples was evaluated within 2 weeks after harvesting. Ten samples which showed wide variations in texture after cooking (i.e. range of low, medium, and high values for penetrometer reading for 1980 crop and highest and lowest values for Kramer maximum shear force for 1981 samples) were chosen from each of the 1980 and 1981 samples for the chemical determinations. The chosen samples were stored in a freezer (−20°C) until used for chemical analysis.

Chemical determinations: Faba beans in each sample (about 300 g) were decoated manually using a sharp scalpel. Seed coats and decoated seeds were ground separately in an analytical mill (IKA Analytical Mill- A 10) to pass a 60-mesh screen. Moisture content was determined by drying at

105°C (AOAC 1975). Phytic acid was determined according to the method of Wheeler and Ferrel (1971). It was precipitated as ferric phytate and the reacted ferric ions were determined colorimetrically using potassium thiocyanate. Phytate phosphorus was calculated using the value of 4:6 (Fe: P ratio). Inorganic phosphorus was determined in the filtrate after precipitation of ferric phytate. Total phosphorus was determined in the ash solution using the colorimetric method of Watanabe and Olsen (1965). Calcium was determined by atomic absorption. All determinations were carried out in triplicate.

Dry faba beans were cooked by autoclaving (seeds: distilled water, 1:4 W/V) at 115.5°C for 2 h. The cooked beans were drained through cheese cloth and left to cool to room temperature. Mean softness score was reported as the number of soft beans in a random sample of ten cooked beans evaluated by ten experienced judges who were chosen by duo-trio test (Kramer and Twigg 1962). One hundred beans of each sample were tested individually by a Universal Precision penetrometer (Hartman 1976) using a 100 -g weight and the mean value is presented as penetrometer reading. The higher the penetrometer reading, the softer the beans.

Since the determination of the penetrometer readings is tedious and time consuming the texture of the 1981 crop samples was measured using the O.T.M.S., i.e., Ottawa Texture Measuring System (Canners Machinery Limited, Ontario, Canada) which was acquired in 1981. This system includes 9005 Mainframe Daytronic Digital Indicator (Model SP-G5P Riken Denshi Co., Ltd., Japan) for recording force-deformation curves. A 100 g sample of drained and cooled cooked beans was placed in a Kramer shear-compression cell (Cat. No. CS - 1) and the maximum (peak) force during the deformation was electronically detected and expressed as Kramer maximum shear force (Kg force/100 g sample). The smaller the force, the softer the beans.

Simple linear correlation coefficients were determined between the texture of the cooked beans and each of phytate, phosphorus contents and phytic acid/Ca ratio.

RESULTS AND DISCUSSION

Results of texture measurements of freshly harvested faba beans (Table 1) showed wide variations among the samples. Standard deviations and coefficients of variability were quite high. Texture of cooked bean samples showed more or less the same trend whether determined subjectively by taste panel (softness score) or objectively by penetrometer or O.T.M.S. Significant correlations were found between the softness score and the

Table 1. Texture measurement of cooked faba bean samples

Sample[a] No.	1980 Crop		1981 Crop	
	Penetrometer Reading	Softness Score	Kramer Maximum Shear Force (Kg/100g)	Softness Score
1	36.7	5.8	115.4	6.7
2	35.6	6.4	134.6	7.2
3	17.8	4.7	157.6	4.1
4	17.6	3.6	117.4	2.0
5	46.8	9.5	122.6	5.4
6	65.9	9.1	52.7	8.6
7	23.0	7.5	54.6	8.9
8	70.3	8.4	56.9	9.4
9	68.3	9.2	64.9	8.8
10	69.7	8.8	61.9	8.0
Range	17.6-70.3	3.6-9.5	52.7-157.6	2.0-9.4
Mean	45.2	7.3	93.8	6.9
Standard deviation	22.0	2.1	39.5	2.4
Coefficient of variability	48.7	28.1	42.1	34.7

a) Cultivars as presented in Tables 2 and 3 for 1980 and 1981 crops.

penetrometer reading (r = 0.83, P<0.01) and between softness score and Kramer maximum shear force (r =-0.77, P<0.01). The negative sign is due to the inverse relationship between Kramer shear force and softness.

Data presented in Tables 2 and 3 show wide variations in phytic acid and phosphorus contents within the same cultivar and during the two years. Griffiths and Thomas (1981) attributed such variation mainly to environmental conditions. Phytic acid and phosphorus were concentrated mainly in the decoated seeds, since the phytic acid and total phosphorus contents of seed coats constituted about 4 to 23% and about 5 to 15.5%, respectively, of those in decoated seeds.

Inorganic phosphorus represented only a small fraction (2 - 4%) of the total phosphorus. However, the mean contents of phytic acid phosphorus of decoated seeds constituted about 30 to 34% of the total phosphorus while those of seed coats constituted from 40 to 47% of the total phosphorus of the seed coats (Table 4). Highly significant correlations were found between total and phytic acid phosphorus of the decoated seeds (r = 0.78, P < 0.01 and r = 0.85, P<0.01 for 1980 and 1981, respectively). Significant correlations were found between phytic acid content and texture of the cooked

Table 2. Phytic acid, phytic phosphorus, inorganic phosphorus, total phosphorus and Ca contents of faba bean seeds (1980 crop; mg/100 g; dry basis)

				Phosphorus Content						
		Phytic Acid		Phytic Acid		Inorganic	Total		Ca Content	
Sample No.	Cultivar	Decoated Seeds	Seed Coat	Decoated Seeds	Seed Coat	Decoated Seeds	Decoated Seeds	Seed Coat	Decoated Seeds	Seed Coat
1	Giza 1	492.5	67.6	152.0	20.8	5.6	614.7	45.3	119	235
2		541.4	56.4	167.1	17.4	6.9	599.1	37.4	89	270
3		289.3	67.5	89.3	20.8	25.3	393.5	61.0	135	217
4		295.2	56.4	91.1	17.4	1.1	430.6	47.3	84	235
5		851.0	33.8	258.5	10.4	3.8	772.6	59.1	99	299
6		386.3	62.1	119.2	19.2	17.7	410.6	39.5	97	294
7		386.0	33.8	116.1	10.4	0.8	473.5	52.2	111	316
8	Giza 2	766.8	79.0	236.7	24.4	4.2	646.6	51.3	67	244
9		492.1	45.1	151.9	13.9	4.3	567.4	45.3	105	480
10		683.4	78.8	211.0	24.3	5.1	442.6	31.5	88	275
Range		289.3-851.0	33.8-78.8	89.3-258.5	10.4-24.4	0.8-25.3	393.5-772.6	31.4-61.0	67-135	217-480
Mean		518.4	58.1	159.6	17.9	7.5	535.2	47.0	99	286
Standard deviation		194.0	16.4	59.1	5.0	7.8	124.3	9.3	19.3	75.2
Coefficient of variability		37.4	28.2	37	28.2	104.7	23.2	19.9	19.4	26.2

Table 3. Phytic acid, phytic phosphorus, inorganic phosphorus, total phosphorus and Ca contents of faba bean seeds (1981 crop; mg/100 g; dry basis)

				Phosphorus Content						
		Phytic Acid		Phytic Acid		Inorganic	Total		Ca Content	
Sample No	Cultivar	Decoated Seeds	Seed Coat	Decoated Seeds	Seed Coat	Decoated Seeds	Decoated Seeds	Seed Coat	Decoated Seeds	Seed Coat
1	Giza 1	276.6	95.6	104.5	36.8	4.2	516.2	72.5	34.6	199.9
2		378.5	45.9	146.7	17.7	7.6	448.4	57.0	45.8	230.4
3		596.9	65.9	229.6	25.4	5.5	587.3	44.6	31.6	304.2
4		767.1	65.1	203.5	25.3	6.6	491.6	49.0	68.7	278.9
5		360.2	44.7	136.3	17.2	6.4	522.0	52.0	53.8	446.7
6	Giza 2	538.7	84.4	289.5	32.4	5.4	764.0	58.4	38.1	244.9
7		345.6	88.6	286.9	34.1	6.5	786.4	73.3	24.9	220.0
8		521.7	102.9	200.7	39.6	8.8	515.3	38.5	42.1	197.3
9		767.4	84.4	130.5	32.4	7.7	373.9	50.8	25.2	165.8
10		389.7	61.3	149.9	23.6	4.1	505.1	64.7	21.9	254.8
Range		276.6-767.4	45.9-102.9	104.5-289.5	14.2-39.6	4.2-8.8	373.9-786.4	38.5-73.3	21.9-68.7	165.8-446.7
Mean		494.3	73.9	187.8	28.5	6.3	551.0	56.1	38.7	254.3
Standard deviation		174.5	20.2	65.2	7.7	1.5	130.3	11.4	14.6	78.9
Coefficient of variability		35.3	27.4	34.7	27.2	24.2	23.6	20.4	37.7	31.0

Table 4. Phytic phosphorus as percentage of total phosphorus of faba bean seeds

	1980 Crop		1981 Crop	
	Phytic Phosphorus		Phytic Phosphorus	
Sample [a] No.	Decoated Seeds	Seed Coat	Decoated Seeds	Seed Coat
1	24.74	46.06	20.24	50.79
2	27.90	46.50	32.72	31.13
3	22.70	34.17	39.09	57.01
4	21.16	36.80	41.00	51.66
5	33.46	17.66	26.11	33.11
6	29.04	48.57	37.90	55.52
7	25.16	20.00	36.50	46.50
8	36.61	47.51	38.96	—
9	26.77	30.70	34.90	63.80
10	47.67	77.30	29.68	36.47
Range	21.16-47.67	17.66-77.30	20.24-41.00	31.13-63.80
Mean	29.58	40.53	33.71	47.33
Standard deviation	7.85	17.09	6.60	11.43
Coefficient of variability	26.53	42.16	19.59	24.16

[a] Cultivars as in Tables 2 and 3 for 1980 and 1981 crops

beans of the 1980 crop ($r = 0.66$, $P < 0.05$ for softness score and $r = 0.72$, $P < 0.01$ for penetrometer reading). However, no significant correlations were found for the 1981 crop.

The calcium content of decoated seeds and seed coats (Tables 2 and 3) varied greatly within cultivars and between years. Seed coats contained much more calcium than decoated seeds. Since Kon and Sanshuk (1981) reported that cooking times of different legumes correlated well with their phytic acid/Ca ratios, this ratio was calculated. No significant correlation was found between it and any of the texture measurements. These data indicate that the phytic acid content does not affect texture of cooked faba beans directly, but rather through interrelations with other constituents such as Ca, Mg, and pectin (Mattson *et al.* 1950; Muller 1967) or starch (Murray *et al.* 1982).

ACKNOWLEDGMENTS

This research was supported by a grant from the International Development Research Center, Ottawa, Canada.

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MINIMIZING ASCORBIC ACID LOSS DURING AIR DRYING WITH A CONSTRAINT ON ENZYME INACTIVATION FOR A HYPOTHETICAL FOODSTUFF

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Recieved for Publication August 15, 1983
Accepted for Publication October 25, 1983

ABSTRACT

The utility of a simulation-optimization approach based on the complex method was demonstrated for a multi-stage drying process. Optimal stage-duration and temperature control were found for minimizing ascorbic acid loss using a literature-derived kinetic model. In addition, enzyme (catalase) inactivation was considered in the staged process. It was desired to control the process so that catalase activity was reduced below a specified level while minimizing ascorbic acid loss. Inequality constraints were also placed on the final retention of moisture and the temperature control range. Due to the large difference in temperature sensitivity at high moisture levels, the optimal configuration maintained the dry- and wet-bulb temperatures very high in a brief first stage to inactivate catalase, followed by milder drying conditions in the final stages to reduce ascorbic acid degradation.

INTRODUCTION

The use of dynamic optimization procedures in food processing operations in general has been limited, and this is true in particular of dehydration. Several attempts have been made to optimize drying processes with respect to minimizing drying time and/or energy costs (Thompson 1967;

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Thygeson and Grossman 1970; Chung 1972; Farmer 1972; Brook 1977; Doe and Menary 1979; Bertin and Srour 1980; Militzer 1981, 1982a, 1982b, 1982c). However, there are few published accounts of maximizing product quality attributes such as color or nutrient retention.

A drying process readily adaptable to optimization is air dehydration (Mishkin *et al.* 1982). The air flow rate and wet- and dry-bulb temperatures may be varied during drying as well as the shape, size, orientation and loading of the product. The optimization scheme may be implemented in a multistage process, in which the control of conditions within each stage is based on the optimal program. An interesting optimization application is one in which several quality factors come into play, each having a different optimal drying program. This problem may be attacked by assigning weights to each factor, and optimizing some derived objective function (e.g. dollar value of weighted quality factors), or it may be solved by optimizing one quality factor, while imposing constraints on other factors (e.g. defining minimum quality levels).

The present study treats the optimization of ascorbic acid retention during air-drying of a hypothetical food, based on a model system for which the drying and reaction kinetics were determined previously. The dynamic optimization which utilized the *complex method,* assumed a multistage process and an additional quality constraint involving inactivation of an enzyme. The enzyme considered was catalase, for which appropriate degradation rate models were available in literature. Control schemes were found for a three-stage drying process which resulted in high retention of ascorbic acid, while inactivating catalase for a hypothetical food system with slab shaped geometry.

MODELS

Figure 1 shows the initial dimensions of the hypothetical food sample. The sample is based on the model system developed previously to study ascorbic acid degradation kinetics (Villota 1978; Villota and Karel 1980a and 1980b). Ascorbic acid degradation could be described by Eq. 1 and 2:

$$-\frac{dC}{dt} = kC \tag{1}$$

where C is the concentration of ascorbic acid (normalized with respect to the initial concentration). The first-order rate constant has moisture and temperature dependence represented by Eq. 2:

$$\ln k = a_1M + a_2T^{-3} + a_3M^3 + a_4M^2T^{-1} + a_5MT^{-2} + a_6M^3T^{-3} + a_7$$

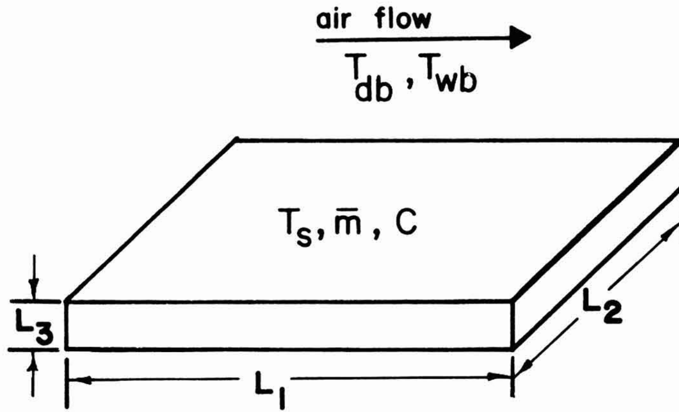

FIG. 1. MODEL SYSTEM USED FOR SIMULATION CELLULOSE SLAB CONTAINING WATER, ASCORBIC ACID AND CATALASE WITH INITIAL DIMENSIONS: $L_1 = 0.6$ cm, $L_2 = 3.4$ cm, $L_3 = 3.5$ cm.

where $a_1 = 17.94$
$a_2 = -2.245 \times 10^8$
$a_3 = -33.33$
$a_4 = 5921$
$a_5 = -1.585 \times 10^6$
$a_6 = 4.711 \times 10^8$
$a_7 = -2.339$

and where M is the moisture content in g/g-sample and T is the absolute temperature in °K. Inactivation kinetics for catalase have been reported by Luyben *et al.* (1980) and are also first-order, and are described by Eq. 3, 4, 5 and 6:

$$-\frac{dC'}{dt} = k'C' \tag{3}$$

$$k' = k'_1 \exp[-E'/RT] \tag{4}$$

$$\ln k'_1 = \ln k_2 - \ln k_3 \exp[-k_4 m] \tag{5}$$

$$E' = E'_1 - E'_2 \exp[-k_4 m] \tag{6}$$

where k' is in $\min^{-1}$
E' is in cal/mole
m is moisture concentration (g/g-solids).

Luyben *et al.* (1980) reported the following values:

$\ln k_2 = 90.36$
$\ln k_3 = 83.07$
$k_4 = 3.699$
$E'_1 = 6.176 \times 10^4$
$E'_2 = 4.916 \times 10^4$

The kinetics for these respective phenomena were determined for different systems. Villota's system was a cellulose-water model system, whereas Luyben took data for cereal products from the literature. For the purposes of this study it was assumed that a particular product contained both ascorbic acid and catalase with kinetics which could be described by these models.

Moisture dynamics were modelled using Fick's Law for unidirectional diffusion:

$$\frac{\partial m}{\partial t} = \frac{\partial}{\partial x}\left(D \frac{\partial m}{\partial x}\right) \tag{7}$$

For simplicity, the diffusion coefficient (D) is assumed independent of moisture concentration. Temperature dependence is given by:

$$D = D_o \exp(-E_D/RT) \tag{8}$$

where D_o = pre-exponential factor (cm^2/s)

E_D = "activation energy" (cal/mol)

Equation 7 has been approximated using a finite difference approach. Figure 2 shows the initial nodal format. For the internal nodes the differential equation describing the i-th volume element is Eq. 9:

$$\frac{dm_i}{dt} = \frac{D}{\delta x_i (S_i)} \left\{ S_{i+1,i} \left[\frac{m_{i+1} - m_i}{\delta x_{i+1,i}} \right] - S_{i,i-1} \left[\frac{m_i - m_{i-1}}{\delta x_{i,i-1}} \right] \right\} \tag{9}$$

If the nodes are close enough it can be assumed that the bulk solids density (S) is uniform in the region represented by Z in Fig. 2, i.e. $S_{i+1,i} = S_i = S_{i,i-1}$. Local shrinkage is taken into account by assuming a linear function of shrinkage with moisture concentration,

$$\delta x_i = \delta x_o \left[P_3 \frac{m_i}{m_o} + P_4\right] \tag{10}$$

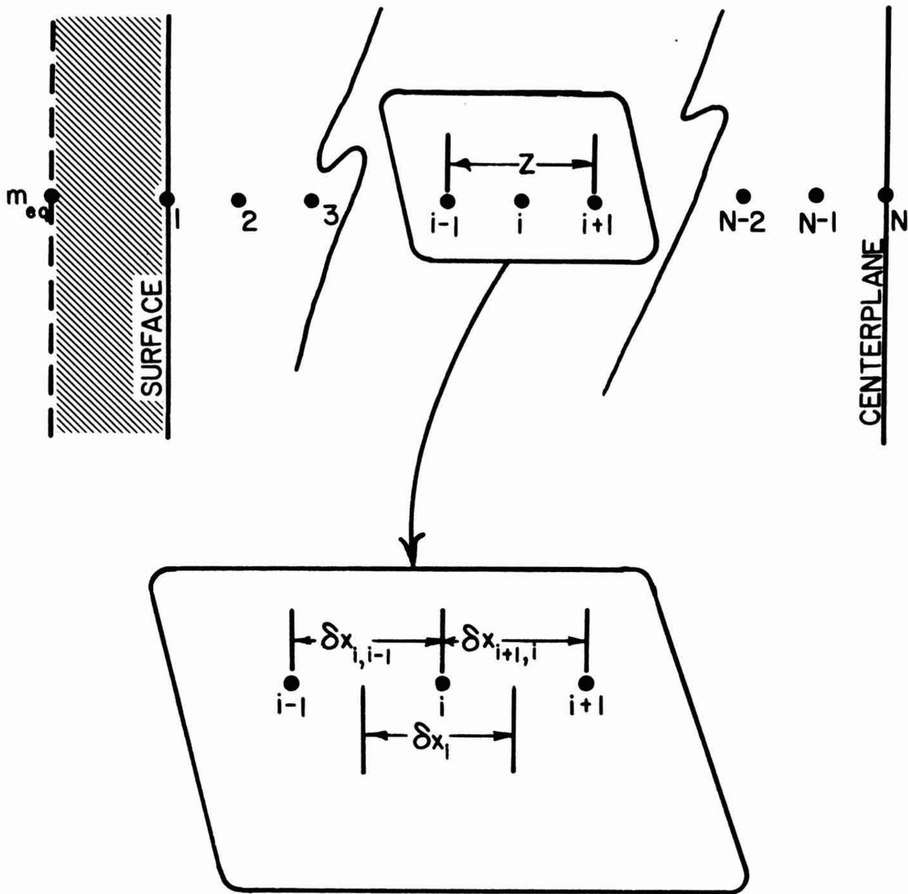

FIG. 2. NODAL FORMAT AND NOTATION USED TO SOLVE THE DIFFUSION PROBLEM USING A FINITE DIFFERENCE METHOD

where δx_o is the initial distance between adjacent nodes, m_o is the initial moisture content, and P_3 and P_4 are parameters. A nearly linear relationship could be expected if shrinkage occurred primarily in the minor dimension of the slab. Lawrence and Scott (1966), and Mishkin (1983) have shown that shrinkage is primarily in the minor dimension for potato slab drying. Again, it can be assumed that in the narrow region Z, $\delta x_{i+1,i} = \delta x_i = \delta x_{i,i-1}$. Equation 9 therefore reduces to Eq. 11:

$$\frac{dm_i}{dt} \simeq \frac{D}{(\delta x_i)^2}[m_{i+1} - 2m_i + m_{i-1}] \qquad (11)$$

For the surface node a fictitious volume element is introduced adjacent to the surface with nodal concentration represented by the equilibrium mois-

ture content of the drying slab (m_e) and transfer characteristics of air (Crank 1975) (see Fig. 2). Equation 12 is the differential equation representing the surface volume element:

$$\frac{dm_i}{dt} \simeq \frac{D}{2(\delta x_1)^2}(m_2 - m_1) - \frac{\beta}{\delta x_1}(m_1 - m_e) \quad (12)$$

where β is the mass transfer coefficient of water in air. It can be simplified by replacing it by an algebraic approximation, Eq. 12:

$$m_1 \simeq \frac{2\delta x_1 \beta m_e + Dm_2}{2\delta x_1 \beta + D} \quad (13)$$

Because $\beta >> D/(2\delta x_1)$, it can be assumed that $m_1 = m_e$, i.e. the surface is at the equilibrium moisture content. For the centerplane node we have:

$$\frac{dm_N}{dt} \simeq \frac{-D}{2(\delta x_N)^2}(m_N - m_{N-1}) \quad (14)$$

where:

$$\delta x_N = \tfrac{1}{2}\delta x_o \,[P_3 \frac{m_N}{m_o} + P_4 \quad (15)$$

The average moisture content $\bar{m}$ is given by:

$$\bar{m} = \frac{(m_1 + m_2)/2 + \sum_{i=2}^{N-1} m_i}{N-1} \quad (16)$$

N is the number of nodes in the finite difference scheme. It should be noted that the volume elements represented by the surface and centerplane nodes are only half the size of the interior volume elements. The nodes are equidistant at the start, but as moisture migrates within the slab, resulting in local shrinkage, the distance between nodes varies, yet the *total solids* content of the respective volume elements remains constant (solids-centered coordinate system).

m_e was determined using the Guggenheim-Anderson sorption equation, and the parametric values reported by Luyben *et al.* (1980).

$$m_e = \frac{(0.01)(RH)(G_2)}{[1 - (RH)][1 + (G_2 - 1)(RH)]} \quad (17)$$

where:

$$G_2 = \exp\left[-\frac{11950}{R}\left(\frac{1}{T} - \frac{1}{313}\right)\right] \tag{18}$$

RH = relative humidity

Most investigators use the Crank-Nicholson method to solve this system of equations in order to insure a stable solution. Stability problems were avoided here by using Gear's implicit integration method (IMSL DGEAR; Gear 1971). The method was convenient because the kinetic equations for ascorbic acid and catalase were easily solved by numerical integration. Accuracy was verified by comparing numerical results to analytical solutions for special cases of the diffusion equation. Insignificant improvement in accuracy was found using more than 10 volume elements, therefore 10 nodes were used in the simulations.

Local kinetics were used to gain more insight into nutrient and enzyme distributions during drying, therefore ascorbic acid and catalase concentrations in each volume element were described by differential equations representing each of the "i" nodes,

$$\left(\frac{dC}{dt}\right)_i = -k\,(m_i, T_s)\,C_i \tag{19}$$

$$\left(\frac{dC'}{dt}\right)_i = -k'\,(m_i, T_s)\,C'_i \tag{20}$$

where T_s is the slab temperature.

The average concentrations of ascorbic acid and of catalase are given by:

$$C_{ave} = \frac{(C_1 + C_N)/2 + \sum_{i=2}^{N-1} C_i}{N - 1} \tag{21}$$

$$C'_{ave} = \frac{(C'_1 + C'_N)/2 + \sum_{i=2}^{N-1} C'_i}{N - 1} \tag{21a}$$

Diffusion of ascorbic acid and catalase within the drying slab was neglected.

The temperature of the drying slab was modelled by a simple heat balance where the temperature was assumed uniform (Lewis no. > 60). To reduce the stiffness of the system, the algebraic approximation (Eq. 22) was used, ignoring the sensible heat term (Mishkin *et al.* 1982):

$$T_s = \frac{\lambda_w m_s}{hA}\left(\frac{d\bar{\bar{m}}}{dt}\right) + T_{db} \tag{22}$$

where the heat of vaporization of water (λ_w) has temperature dependence (Luyben *et al.* 1980),

$$\lambda_w = 744 - 0.537\ (T_s + 273)\ \text{cal/g} \tag{23}$$

As described by Mishkin *et al.* (1982), due to shrinkage the heat transfer coefficient (h) and the surface area (A) are variable during drying therefore the quantity "hA" has been modelled as a linear function of moisture,

$$hA = A_o\ (P_1\bar{\bar{m}} + P_2) \tag{24}$$

where $P_1 = 0.0026$
$P_2 = 0.043$

The rate of moisture loss ($d\bar{\bar{m}}/dt$) is described by Eq. 25:

$$\frac{d\bar{\bar{m}}}{dt} = \frac{dm_N/2 + \sum_{i=2}^{N-1} dm_i/dt}{N-1} \tag{25}$$

The parameters in Eq. 8, 10, and 15 were estimated using least squares techniques, and drying data of Villota (1978):

$D_o = 74$
$E_d = 10840$
$P_3 = 0.203$
$P_4 = 0.797$

OPTIMIZATION USING THE COMPLEX METHOD

The complex method of multivariable, constrained minimization was used to determine the optimal configuration for the three-stage drying

process with constant drying conditions in each stage. The total drying time (t_f) was specified. The independent variables were the temperatures in each of the three stages (T_{db_1}, T_{db_2}, T_{db_3}), the relative humidity in each stage (RH_1, RH_2, RH_3), and the relative time duration of each stage (t_f, t_{f_2}). The time duration "t_{f_1}" is for the first dryer stage and "t_{f_2}" the residence time in the second. Since the total drying time is specified the residence time in the third stage is not independent. In practice T_{wb} would be controlled along with T_{db}. It was convenient to use RH here to facilitate easy evaluation of the surface boundary condition via the sorption equation (Eq. 17). Psychrometric data can easily be used to determine the T_{wb} needed (in conjunction with T_{db}) to obtain the necessary RH determined by the optimization method. The objective function used was:

$$\min J = -C_{ave}(t_f) \tag{26}$$

An implicit constraint was imposed on the final catalase concentration: C'_{ave} ($t_f < 0.001$ (i.e. 0.1% retention). This is analogous to the constraints placed on maximum final spore counts in thermal processing of canned foods. An inequality constraint was also placed on the final moisture content of the slab ($M(t_f) \leq 0.05$ g/g of solids) realizing that the constraint would be active at the optimum. The temperature in each stage was constrained $55°C \leq T_{db} \leq 85°C$.

The method used to solve this problem is defined by Umeda *et al.* (1972) and is nearly identical to the method used by Mishkin *et al.* (1982). It is a simulation-optimization method using the complex method.

RESULTS

Figures 3 and 4 show the moisture and temperature sensitivities of the first order rate constants for ascorbic acid degradation and catalase inactivation, respectively. The Arrhenius plot has been used in Fig. 5 to help illustrate the contrasting temperature sensitivities of ascorbic acid and catalase at the initial moisture level of 2.5 g/g-solids. At high moisture levels the rate constant for catalase inactivation is much more sensitive to temperature than that for ascorbic acid, as indicated by the larger negative slope in Fig. 5. This behavior is not unusual for enzymes. In fact, protein denaturation in general has a high activation energy, with sensitivity decreasing with water activity. Figures 6 and 7 show the simulated final retention profiles for catalase and ascorbic acid for slabs dried six hours at 55 and 65°C, respectively. The consequences of this contrast in temperature sensitivity are evident. This small difference in air tempera-

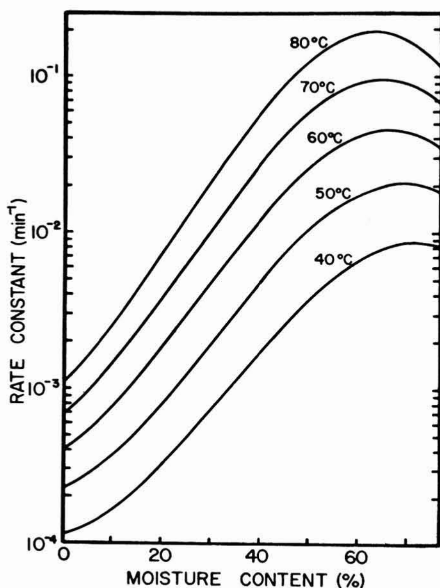

FIG. 3. MOISTURE AND TEMPERATURE DEPENDENCE OF THE FIRST-ORDER RATE CONSTANT FOR ASCORBIC ACID DEGRADATION

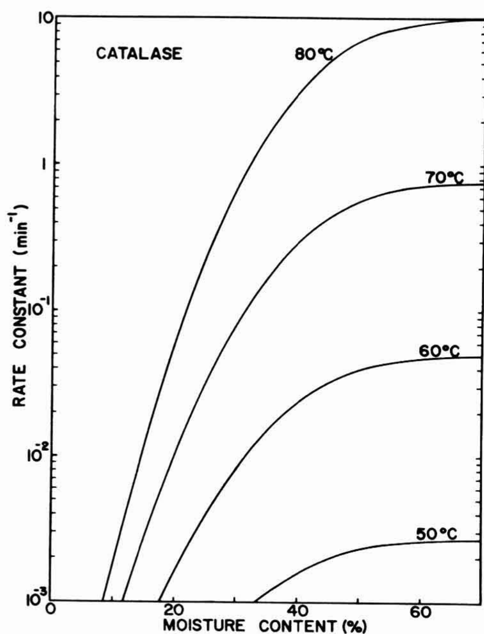

FIG. 4. MOISTURE AND TEMPERATURE DEPENDENCE OF THE FIRST-ORDER RATE CONSTANT FOR CATALASE INACTIVATION

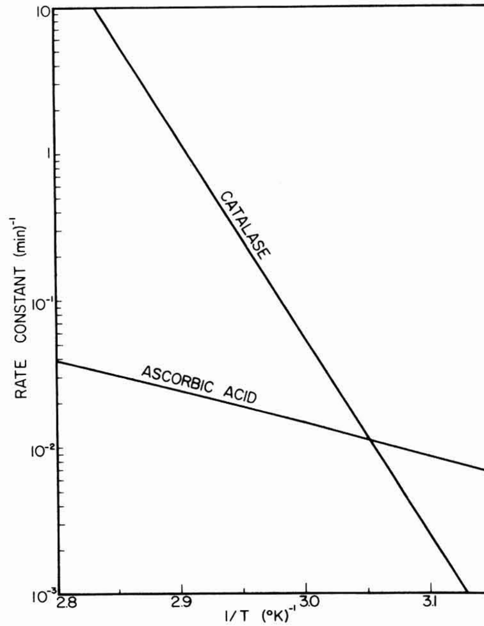

FIG. 5. ARRHENIUS PLOT, SHOWING DIFFERENCE IN TEMPERATURE SENSITIVITY BETWEEN ASCORBIC ACID AND CATALASE AT THE INITIAL MOISTURE CONTENT, 2.5 g/g-solids

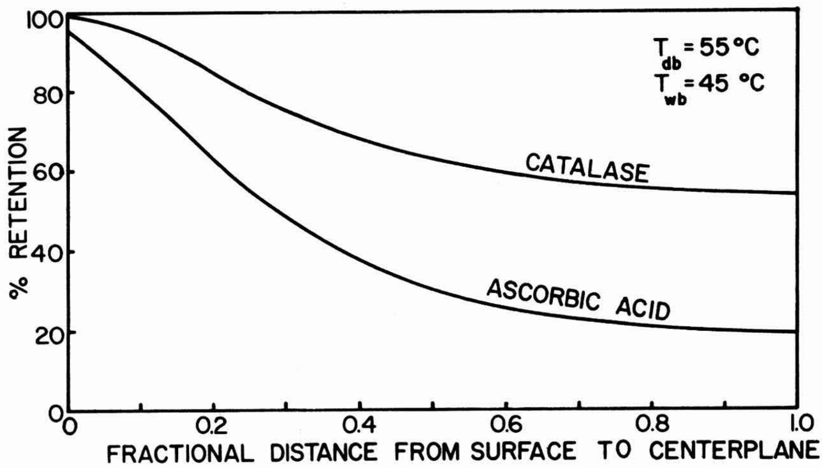

FIG. 6. SIMULATED FINAL RETENTION PROFILES FOR ASCORBIC ACID AND CATALASE, FOR A DRYING PROCESS AT 55°C AND FINAL MOISTURE CONTENT, 0.05 g/g-solids

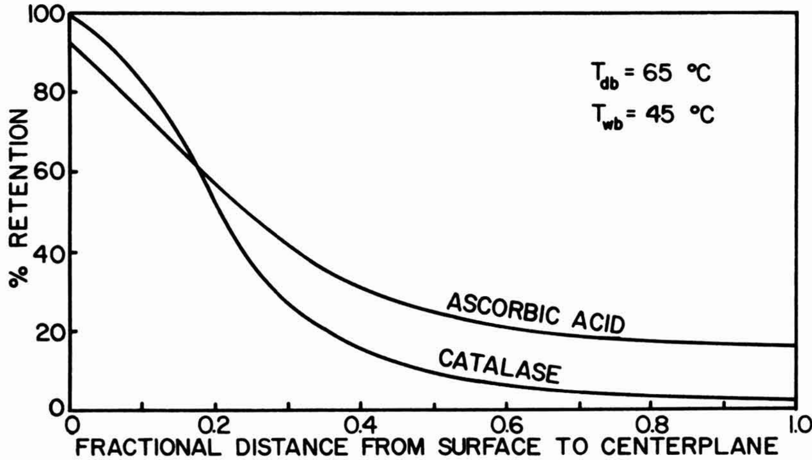

FIG. 7. SIMULATED FINAL RETENTION PROFILES FOR ASCORBIC ACID AND CATALASE, FOR A DRYING PROCESS AT 65°C AND FINAL MOISTURE CONTENT, 0.05 g/g-solids

ture results in a significant decrease in catalase retention while only slightly altering the ascorbic acid retention profile. Figure 8 summarizes this point by showing the average retentions (see Eq. 21) after six hours of drying as a function of air temperature. Both ascorbic acid and catalase become more stable as the moisture concentration decreases which is clear from the final concentration profiles in Fig. 6 and 7. The surface of the slab dries rapidly (see Fig. 9) stabilizing surface catalase against inactivation. This residual catalase causes the retention curve in Fig. 8 to level of above 70°C.

Mishkin *et al.* (1982) found optimal temperature control profiles for maximizing ascorbic acid retention in a batch drying process using average moisture kinetics for a cellulose slab model system. For the three-stage drying process with constant control in each stage and using local moisture kinetics, the complex method may be used to find the control scheme which maximizes the final retention of ascorbic acid. Figure 10 shows the optimal configuration for a 330 min process. This control scheme is optimal for ascorbic acid retention without a constraint on the inactivation of catalase. Final moisture retentions were constrained ($M(t_f) \leq 0.05$ g/g-solids). At first glance, the temperature in the first stage seems surprisingly high, but the high rate of drying keeps the sample temperature low as illustrated in Fig. 11. Obviously, the relative humidity would be kept as low as possible in all three stages in this case, to dry the slab quickly and thus stabilize ascorbic acid. These results are useful for comparison to the process in which an implicit constraint is placed on catalase inactivation.

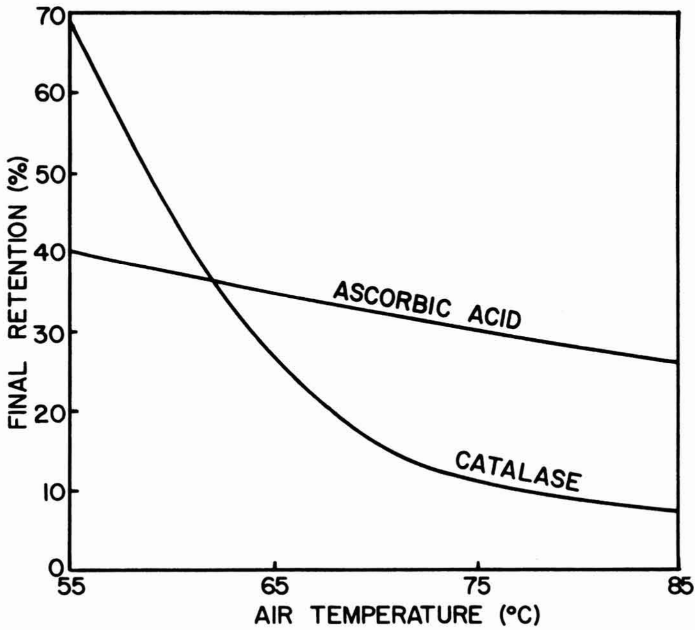

FIG. 8. AVERAGE FINAL RETENTIONS OF ASCORBIC ACID AND CATALASE AS A FUNCTION OF DRYING TEMPERATURE

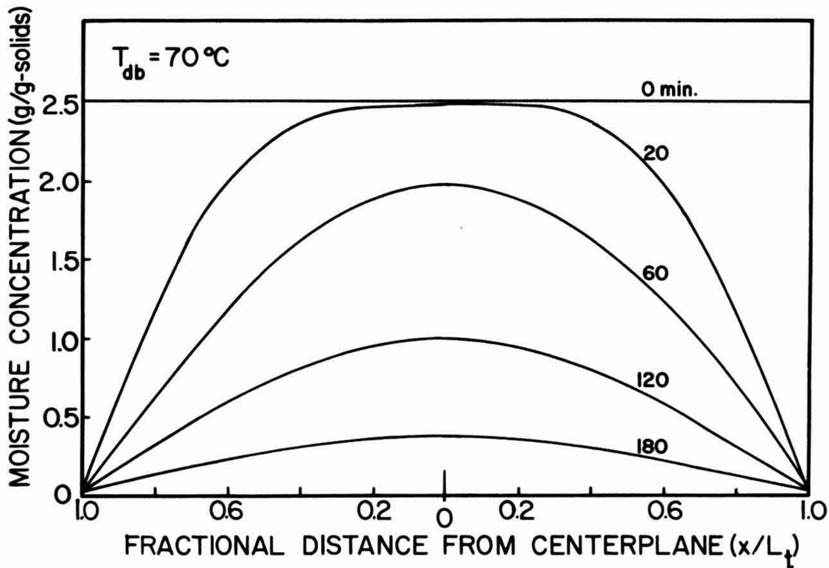

FIG. 9. TIME VARYING MOISTURE PROFILES IN THE DRYING SLAB

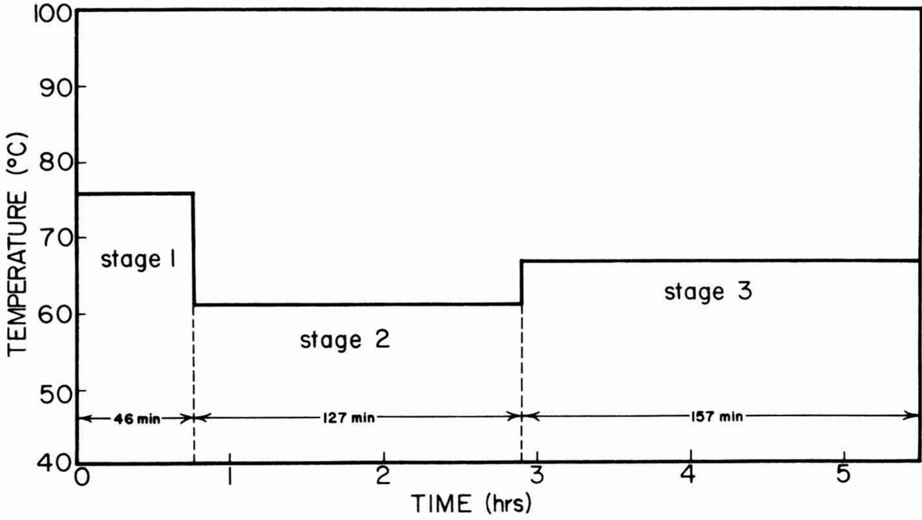

FIG. 10. OPTIMAL 3-STAGE DRYING PROCESS FOR MINIMIZING ASCORBIC ACID DESTRUCTION FOR A 330 MIN PROCESS

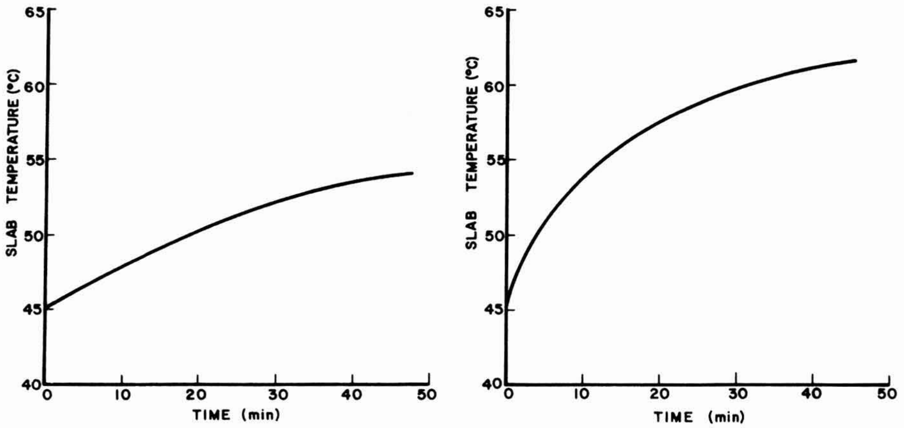

FIG. 11. TIME VARYING SLAB TEMPERATURE CORRESPONDING TO THE 1ST-STAGE DRYER CONTROL OF FIG. 10

In view of the contrasting moisture and temperature sensitivities of ascorbic acid and catalase the optimal configuration for the three stage drying process with T_{db} and RH decision in each stage and implicit constraint on C'_{ave} (t_f) is shown in Fig. 12 for the 330 min process. The first stage is operated at a high temperature and 100% RH for a brief period which inactivates most of the catalase. Note that the slab temperature would track T_{db} under these conditions. The optimization results indicated that the final two stages be lumped into a single stage at 66°C. The first stage is primarily responsible for satisfying the implicit constraint on catalase inactivation while the remainder of the process must act to satisfy the constraint on final moisture retention. As expected, at the optimal solution, both constraints are active, i.e. the final moisture content is 0.05 g/g-solids and there is a 99.9% inactivation of catalase. At the end of the first stage, catalase has already been reduced by 99.6% while only about 3% of the ascorbic acid has degraded. This is after only 50 s of treatment. In the optimal three stage process where catalase inactivation was ignored, there was only an 83% reduction in catalase activity for the entire drying process. No significant ascorbic acid damage resulted from the additional constraint due to catalase inactivation. The final retention was only slightly decreased for the catalase-constrained process compared to the unconstrained case (1% reduction).

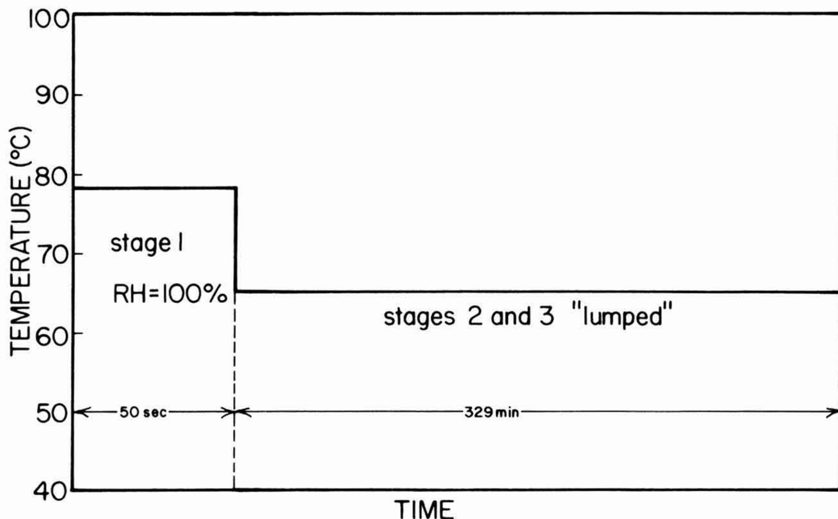

FIG. 12. OPTIMAL 3-STAGE DRYING PROCESS FOR MINIMIZING ASCORBIC ACID DESTRUCTION WITH CONSTRAINED FINAL CATALASE ACTIVITY FOR A 330 MIN PROCESS

The optimal configuration is not surprising. The temperature and humidity are elevated during the first stage taking advantage of the large temperature sensitivity of the catalase. It is necessary that the surface be kept moist during this "enzyme inactivation" phase so that surface catalase remains unstable. Having already destroyed most of the catalase, the remainder of the process may be run at the lower temperature and humidity to preserve ascorbic acid. These results are strictly analogous to the high-temperature short-time (HTST) thermal processes. Bacterial spores, for example, exhibit higher temperature sensitivity than nutrients in canned foods. By operating retorts at high temperatures for brief periods the number of viable bacteria may be drastically reduced while preserving much of the nutritional quality.

The optimal configuration found in this study is equivalent to the standard industrial practice; blanching to inactivate enzymes followed by drying. These results confirm that existing practices are near optimal, at least for the quality factors considered here. However, the primary objective of this study was to demonstrate the utility of the complex method for multistage processes.

CONCLUSION

The complex method is an effective approach for determining optimal control configurations for multi-stage drying processes. It is feasible to control such processes so that nutrients may be preserved while inactivating undesirable enzymes. Greater insight can be attained by studying local moisture effects on degradation kinetics of quality factors. Although the methods have been demonstrated for an idealized geometry for the drying material, the approach is applicable to much more complex situations such as fluidized beds. In such a case, one may choose to model the "average particle" of a material with specified particle-size distribution.

ACKNOWLEDGMENT

This work was supported in part by grants ENG-7824342 and CPE-8104582 from the Division of Engineering, National Science Foundation.

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BOOK REVIEWS

Food Additives Recent Developments, J. C. Johnson, Noyes Data Corporation, Park Ridge, N.J. 412 pp. 1983. $45.00.

The title of this book needs one word — "Patent". The contents in this volume is based on U. S. patents, issued between January, 1979 and July, 1982 that deals with food additives.

To my knowledge there is no other book or major publication similar to this in the food industry. This book is a must for those involved in innovative research linked to patents related to food additives. The information presented here fills a gap. For many industrial and non-industrial people, patent information is critical and is usually not covered in journal literature. The major benefits of this book is that it eliminates legal jargon and juristic phraseology and lets the scientist "get down" to science.

The book covers some 247 food additives or disclosed in 258 patents. The book does not include patents as flavor, colors, sweetener and nutritive additives. Stabilizers which maintain freshness and retard spoilage are described in 57 patents comprising the first two chapters. Additives which improve the texture or processing of foods are covered in the chapters on vegetable gums, emulsifiers and modified starches.

The preparation and use of protein additives and substitutes are disclosed by the 57 patents of the next two chapters. Soy, caseinate, yeast, gluten and other materials serve as the source of the proteins.

The remaining two chapters describe other additives such as fat substitutes, acids, and salts, leavening agents, low calorie material, yeast products, etc.

Because the book covers so many patents, the patents are very condensed and the reader if interested in more detail needs to obtain the patent him or herself. Nevertheless, research personnel, or others wishing to broaden their knowledge of recent patent developments, will find this book an invaluable source.

Edible Oils and Fats-Developments Since 1978 S. Torrey, Noyes Data Corporation, Park Ridge, N.J. 402 pp. 1983. $44.00.

This book is a collection of U.S. patents issued from June 1978 through April 1982, that deals with edible oils and fats.

What this book does is bring together in a descriptive format summaries of patents pertinent to those people who are working with edible fats and oils.

This book covers about 266 patents most of which concern themselves with the food industry but some are related to applications in the pharmaceutical industry. The areas which are covered by the patents are

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extraction and fractionation processes, purification processes, modifying properties of fats and oils, margarines and spreads, cooking and salad oil, confectioner's fats, dairy products and dairy product substitutes, salad dressings and pan release agents, meat, meat analysis and animal feeds, emulsifiers for fat-containing food products, additional fat-containing food products. An additional plus is that the book also contains an index by company, an index by inventor and an index by U.S. patent number.

Each patent has a brief introduction followed by a technical information section. This is advantageous to both scientists and non-scientists or those who are familiar with the research areas or those with just a passing interest. If one needs more detail on a particular patent it is suggested that it be obtained through the patent office since this book only contains short and concise descriptions. What is nice about this book is that it can serve as an invaluable resource for those in all product development areas, since there are few food products in the U.S. which are processed or manufactured without any fat or oil.

Innovative research departments and others interested in new ideas will find this book to be invaluable.

M.K. SCHMIDL

F
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P
JOURNALS AND BOOKS IN FOOD SCIENCE AND NUTRITION

Journals

JOURNAL OF NUTRITION, GROWTH AND CANCER, G. P. Tryfiates

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1A. TITLE OF PUBLICATION	1B. PUBLICATION NO.	2. DATE OF FILING
Journal of Food Processing & Preservation	4 5 6 4 7 0	Oct. 1, 1983

3. FREQUENCY OF ISSUE	3A. NO. OF ISSUES PUBLISHED ANNUALLY	3B. ANNUAL SUBSCRIPTION PRICE
Quarterly	4	$65.00

4. COMPLETE MAILING ADDRESS OF KNOWN OFFICE OF PUBLICATION *(Street, City, County, State and ZIP Code) (Not printers)*

155 Post Road East, Suite 6, POB 71, Westport, Fairfield, CT 06881

5. COMPLETE MAILING ADDRESS OF THE HEADQUARTERS OF GENERAL BUSINESS OFFICES OF THE PUBLISHER *(Not printer)*

155 Post Road East, Suite 6, POB 71, Westport, Fairfield, CT 06881

6. FULL NAMES AND COMPLETE MAILING ADDRESS OF PUBLISHER, EDITOR, AND MANAGING EDITOR *(This item MUST NOT be blank)*

PUBLISHER *(Name and Complete Mailing Address)*

John J. O'Neil, 155 Post Road East, Suite 6, POB 71, Westport, CT 06881

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Food & Nutrition Press, Inc.	155 Post Road E. S.#6, POB 71, Westport CT 06881
Technomic Publishing Co.	265 Post Road West, Westport, CT 06880
(Melvyn A. Kohudic)	265 Post Road West, Westport, CT 06880
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