F
N P
✓

JOURNAL OF FOOD PROCESSING AND PRESERVATION

D.B. LUND
EDITOR

JOURNAL OF FOOD PROCESSING AND PRESERVATION

Journal of
FOOD PROCESSING
and
PRESERVATION

EDITORIAL

This past year has seen continued interest in the Journal of Food Processing and Preservation. Excellent cooperation from our team of authors, publisher (especially Ms. Kathy O'Neil), reviewers (see list below), and my secretary, Mary Wojciechowski, continue to bring an outstanding Journal of quality and vitality to the readers. I want to thank Editorial Board members William Breene (University of Minnesota), Frank Busta (University of Minnesota), Jerry Cash (Michigan State University), Barry Swanson (Washington State University), and J.H. VonElbe (University of Wisconsin), for their service on the Editorial Board. Each will continue on the Editorial Board for another three-year term.

There is currently no delay for publication once papers have been accepted for publication. We continue to seek papers in the area of "computer codes and their applications" and "databank". Please consider the Journal of Food Processing and Preservation for your next paper.

Reviewers for 1994:

DARYL LUND
Editor

CONTENTS

ANTIOXIDATIVE EFFECT OF ISUBGOL IN MODEL AND IN LIPID SYSTEM[1]

RAJESH L. MEHTA[2], JOSEPH F. ZAYAS[2] and SHIE-SHIEN YANG[3]

[2]*Department of Foods and Nutrition, Justin Hall*

and

[3]*Department of Statistics*
Kansas State University
Manhattan, KS 66506

ABSTRACT

Eight separate solvent systems were used to determine which was most effective and rapid for extraction of antioxidants from seeds of isubgol (Plantago ovata); *methanolic extracts showed the highest antioxidative power. Effectiveness was tested in a model system of linoleic acid and in a lipid system of soybean oil stored at 32C and 60C and heated at 180C. The methanolic extracts of isubgol tested in emulsified linoleic acid showed no marked decrease in oxidation compared to the control, as measured by coupled oxidation with β-carotene, conjugated dienes (CD) values, and TBA-test. The extracts in soybean oil did not produce significantly lower peroxide values, lower CD, or higher 18:2/16:0 ratios than the control during storage and heating tests. Thus, isubgol is not a potential source of natural antioxidant.*

INTRODUCTION

Food deterioration during storage is caused by lipid oxidation and hydrolysis (Allen and Hamilton 1983). Oxidation of lipids resulted in changes in food composition like formation of volatile odoriferous and color compounds (Pokorny 1981), changes in textural properties, decrease in nutritive value (Farag *et al.* 1989), and oxidation of cholesterol (Eriksson 1982). Synthetic antioxidants suppress the peroxide formation and increase shelf-life of foods (Chang *et al.* 1977) and also preserve their nutritive value. The most commonly

439

used antioxidants at the present time are BHA, BHT, and TBHQ. However, consumers prefer food with natural additives because it is generally believed to be safer and more nutritious. Therefore, a search for natural antioxidants as alternatives to synthetic ones is highly recommended. Several sources of natural antioxidants with characteristic properties are known, including plants and microorganisms. Many of them were identified as promising sources of natural antioxidants like rosemary (Shai *et al.* 1985), β-carotene (Burton and Ingod 1984) and ginger rhizome (Lee *et al.* 1986). The need for safe, efficient, widely utilized, and easily available natural antioxidants continues to exist.

The present study was conducted to determine and compare the antioxidative activity of isubgol *(Plantago ovata)*, with that of BHT and TBHQ. *P. ovata* is important for its seeds (Isubgol), which are widely used in medicine. The seeds are considered demulcent, stimulant, diuretic and tonic, and are used as a remedy for dysentery and diarrhea. The seed oil is suitable for edible purpose with an agreeable odor and a taste resembling that of walnut.

MATERIALS AND METHODS

Raw Materials

Isubgol seeds were obtained from GSCSC Ltd., Gandhinagar, Gujarat, India, and utilized for extraction of substances with antioxidative properties. Refined, bleached, and deodorized (RBD) soybean oil without any antioxidants added during processing was obtained from Kraft Food Ingredients, Memphis, Tennessee, and was stored in amber bottles under inert gas at −25C until experiments and analysis.

Procedure

The procedures of Duve and White (1991) and Farag *et al.* (1989) were followed for extraction and identifying and testing antioxidative activity of the extracts.

Extraction. The seeds were cleaned, air dried at 40C for 48 h, then finely ground (1 mm) in a mill. A 100 g of each ground sample was extracted in a Soxhlet extractor with 250 ml of solvent for 6 days. The residues were air dried at room temperature for 12 h and extracted with solvents as shown in Fig. 1.

All extracts were concentrated in a vacuum in a rotary evaporator at 40C. All operations were run in the dark to protect the extract from light-induced isomerization.
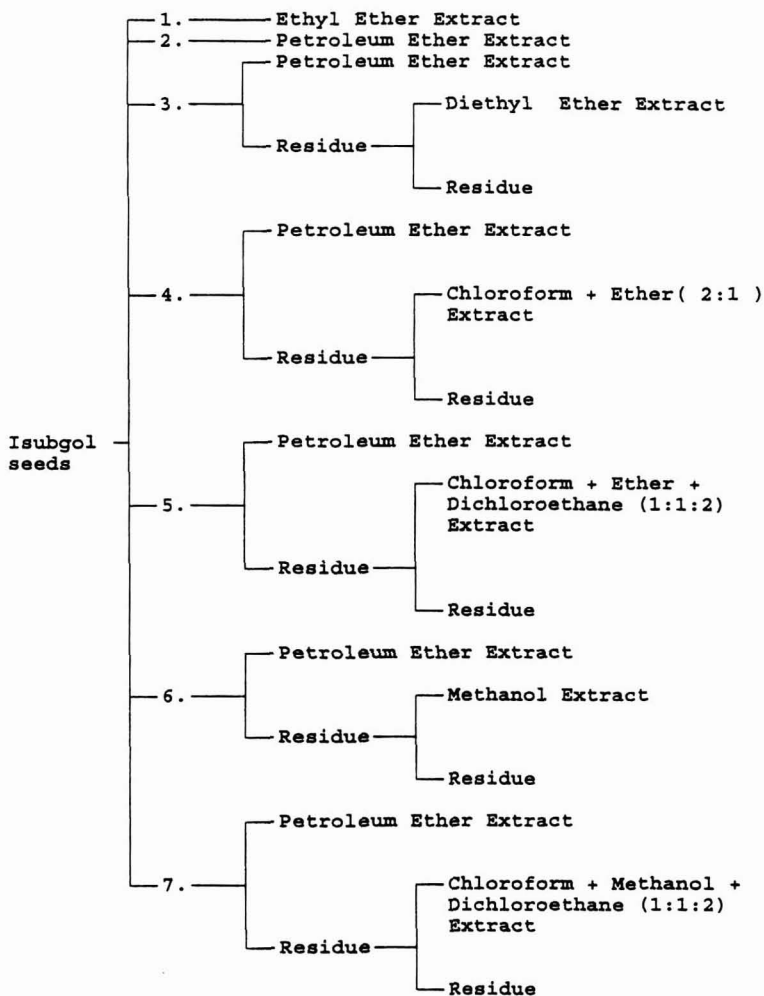
FIG. 1. EXTRACTION SCHEME FOR ISUBGOL SEEDS

Rapid evaluation of antioxidant effectiveness among extracts was performed by thin layer chromatography (TLC) tests. The procedures utilized by Daniels and Martin (1967) and Pratt and Miller (1984) were followed. After activation at 100C for 1 h, TLC plates (0.25 mm, precoated with Silica gel G obtained from Fisher Scientific, Itasca, IL) were streaked with 200 μl of extract and developed in the upper phase of chloroform/ethanol/acetic acid (98:2:2). After development, the plates were sprayed with a solution of 9 mg β-carotene dissolved in 30 ml chloroform, to which two drops of linoleic acid and 60 ml of ethanol were added. The sprayed plates were exposed to daylight for 6 h. The intensity of the resulting orange color corresponded to the relative antioxidant activity of the extract (Marco 1968; Taga et al. 1984).

Experimental Procedure for Model System of Linoleic Acid in an Aqueous Medium. Three methods were used to follow the oxidation of linoleic acid: (1) coupled oxidation with β-carotene (Marco 1968), (2) conjugated diene formation (Allen et al. 1979), and (3) TBA-test (Ronald and Ronald 1991).

β-carotene was dissolved in chloroform (0. 05%). A 10 ml sample was pipetted and mixed with linoleic acid (ca. 1.4 g) and Tween 20 (1 ml, 0. 02%). The solvent was evaporated, then 500 ml deionized water was added and emulsification was achieved by agitation using an ultrasonic bath. The stock solutions of emulsified solvent extracts have been prepared. Tween 20 (0.25 ml, 0.2%) was mixed with methanolic extracts of isubgol (which showed highest antioxidative activity in TLC test) at different levels in a volumetric flask (50 ml), and the mixture was made up to the mark with deionized water and emulsified by agitation using an ultrasonic bath for 15 min. Then the reaction mixture was prepared by adding emulsified stock solution to emulsified linoleic acid-β-carotene and mixing. Similarly, BHT was added to emulsified linoleic acid-β-carotene to compare the antioxidant efficiency.

Coupled Oxidation of Linoleic Acid-β-Carotene Method. Aliquots (0.2 ml) from reaction mixture were taken and diluted with ethanol (3 ml, 99%) at 1-h intervals, until complete disappearance of β-carotene's orange color, and vortexed for 30 s. Absorbance was recorded at 462 nm against a blank containing solvent.

Conjugated Diene Formation Method. Aliquots (0.1 ml) were taken at 1-day intervals from the reaction mixture, diluted with methanol (3 ml), and vortexed. Absorbance was measured at 232 nm.

TBA-Test. The sample (100 mg) was made up to 25 ml in a 25 ml volumetric flask with 1-butanol and mixed. A 5.0 ml diluted sample and TBA reagent (200 mg of 2-thiobarbituric acid in 100 ml 1-butanol, filtered, stored at

4C for not more than 7 days) were pipetted into a dry, stoppered test tube and placed in a water bath at 95C for 120 min. After cooling, light absorbance was measured at 532 nm against a blank containing all the reagents except linoleic acid. Samples were drawn 1-day intervals.

Experimental Procedure of Real Lipid System Using RBD Soybean Oil (Without Antioxidants). Concentrated, extracted portions of solvent and synthetic antioxidants (BHT and TBHQ) were dispersed in RBD soybean oil. After being mixed and stirred for 30 min at 50C, samples were stored under nitrogen at −18C until tested.

Storage Test. Levels of 0.02%, 0.05%, 0.1% and 0.2% by weight for the methanolic extract having the highest antioxidative power and 0.02% for BHT and TBHQ were tested. A 1000 ml portion of each sample, mixed with antioxidants, was stored at controlled temperatures of 32C and 60C. The samples were analyzed every 2 days for 20 days. Peroxide values were determined according to AOCS, Cd 8-53 (AOCS 1987).

Heating Tests. Methanolic extracts of isubgol (MEI) were tested at frying temperature (180C) by adding levels of 0.02%, 0.05%, 0.1%, and 0.2% by weight to 1000 ml RBD soybean oil. BHT and TBHQ were tested at the legal limit of 0.02%. Heating was carried out at 180C for 10 h/day for 14 days. Oil was sampled every 2 days and stored under nitrogen at −18C until analyzed by the gas chromatography (GC) method (Slover and Lanza 1979) and conjugated diene values (Ti 1a-64 AOCS 1987).

Statistical Analyses. The experimental design was completely randomized and six replications per treatments were randomly and independently processed. Data analysis and graphic plotting were done with SAS programs (SAS 1985). Differences were determined by comparing treatment means using least significant difference (LSD) multiple comparison method and the procedure of Student, Newman (1939), and Keuls (1952) (SNK method). Analysis of variance and regression analysis were also used to analyze the data (Steel and Torrie 1980).

RESULTS AND DISCUSSION

Coupled Oxidation of Linoleic Acid-β-Carotene Method

This method was selected as a preliminary and fast test to distinguish the antioxidant activity of certain compounds, using added β-carotene as a marker
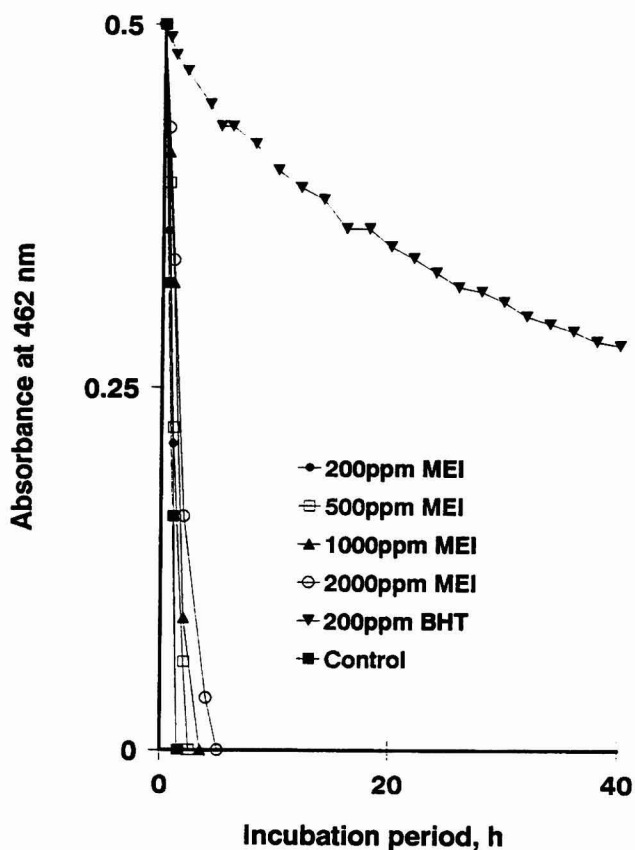
FIG. 2. OXIDATION OF EMULSIFIED LINOLEIC ACID-β-CAROTENE
TREATED WITH METHANOLIC EXTRACTS OF ISUBGOL (MEI) AND BHT

for the oxidation reaction of linoleic acid in an aqueous medium (Marco 1968; Farag *et al.* 1989; Taga *et al.* 1984). Thus, the disappearance of color of β-carotene was entirely dependent on the hydroperoxide formation, which increased with time. Six replications for each treatment were carried out and averaged for plot. The trend for bleaching of β-carotene coupled with oxidation of linoleate systems is shown in Fig. 2. The time required for the complete disappearance of β-carotene was measured. As shown in Fig. 2, the time required for complete bleaching of β-carotene was highest for the control, which had no antioxidant to decrease the oxidation of linoleic acid. The lowest time for complete bleaching of β-carotene was observed for BHT. Methanolic

extracts of isubgol (MEI) with increased concentrations showed few antioxida-
tive properties, and the extent of antioxidative activity was not much dependent
on the concentration of crude extracts.
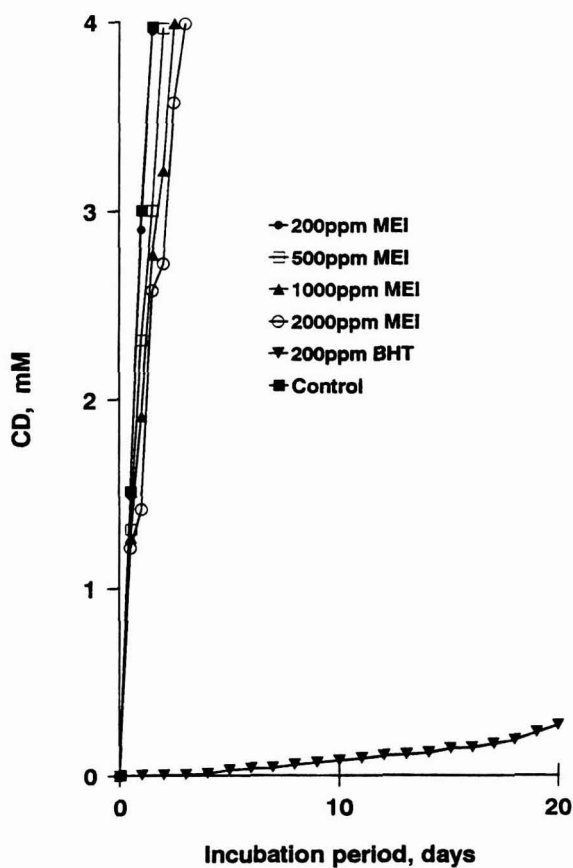
FIG. 3. CONJUGATED DIENE (CD) HYDROPEROXIDE FORMATION
BY EMULSIFIED LINOLEIC ACID TREATED WITH METHANOLIC
EXTRACTS OF ISUBGOL (MEI) AND BHT

Conjugated Diene Formation Method

Oxidation of linoleic acid was followed by measuring conjugated diene (CD)
values in samples treated with antioxidants. In order to compare the antioxida-
tive behavior of different concentrations of MEI with BHT, data obtained for six

replications were averaged and plotted with time as shown in Fig. 3. As shown in Fig. 3, there was no difference in trends for the formation of conjugated diene between different concentrations of MEI and control. This indicates poor oxidative properties of extracts of isubgol and poor effect on the oxidative stability of linoleic acid in an aqueous medium. BHT showed the highest antioxidative power among all treatments.
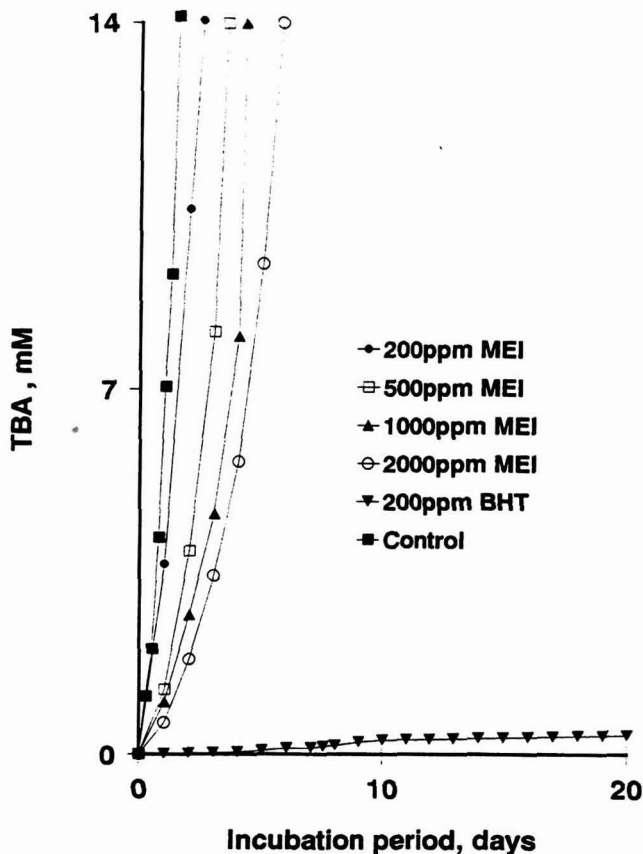
FIG. 4. THE EFFECT OF METHANOLIC EXTRACTS OF ISUBGOL (MEI) AND BHT ON THE SECONDARY OXIDATION PRODUCTS OF EMULSIFIED LINOLEIC ACID

TBA-Test

Oxidation of linoleic acid was followed by measuring the TBA values resulting from formation of secondary products such as aldehydes, ketones, etc.

The data obtained from six replications of each treatment were averaged and plotted against time as shown in Fig. 4. Increased concentrations of MEI had little preventive effect on decreasing the formation of secondary oxidation products by linoleic acid oxidation in an aqueous medium, which indicates poor antioxidative activities of crude MEI.
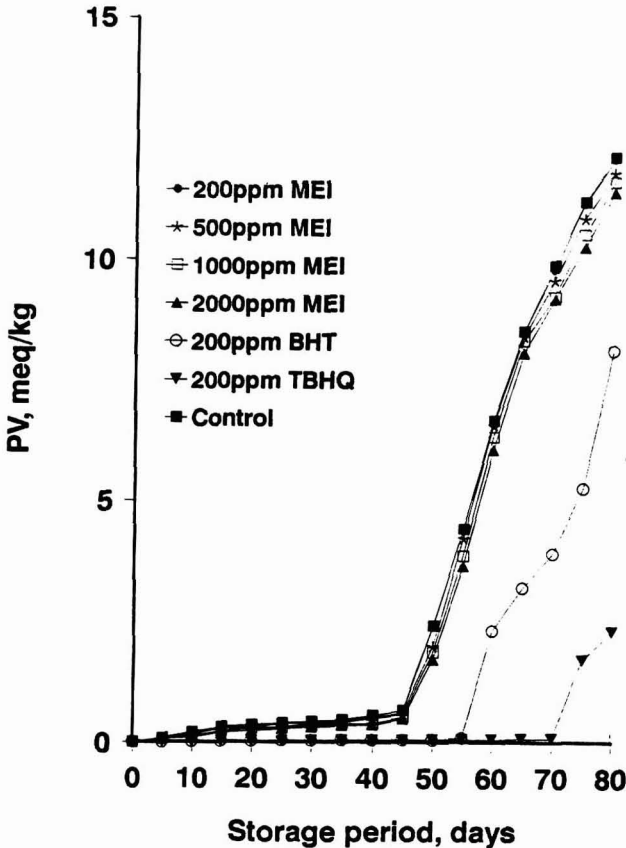
FIG. 5. PEROXIDE VALUE (PV) OF SOYBEAN OIL WITH ADDED METHANOLIC
EXTRACTS OF ISUBGOL (MEI), BHT AND TBHQ DURING STORAGE AT 32C

Real Lipid System Using RBD Soybean Oil

Storage Test. Average peroxide values (PV) of six replications for each treatment at storage temperatures of 32C and 60C were plotted against days of heating as shown in Fig. 5 and Fig. 6, respectively. Comparisons among

treatments also were made from peroxide formations. Figures 5 and 6 showed a typical pattern in the rise of PV for all treatments at 32C and 60C storage. The control (without added antioxidants) had the highest peroxide formation among all treatments during storage at 32C and at 60C, indicating that it oxidized quickest (Fig. 5 and Fig. 6). No significant differences occurred among the controls and of the oils containing MEI at 32C. The significantly lower peroxide formation for different concentrations of MEI than for the control at 60C storage indicated little antioxidative power of the extracts. TBHQ demonstrated the highest antioxidative power to prevent soybean oil oxidation. Increased concentrations of MEI did not stabilize oxidation of soybean oil.
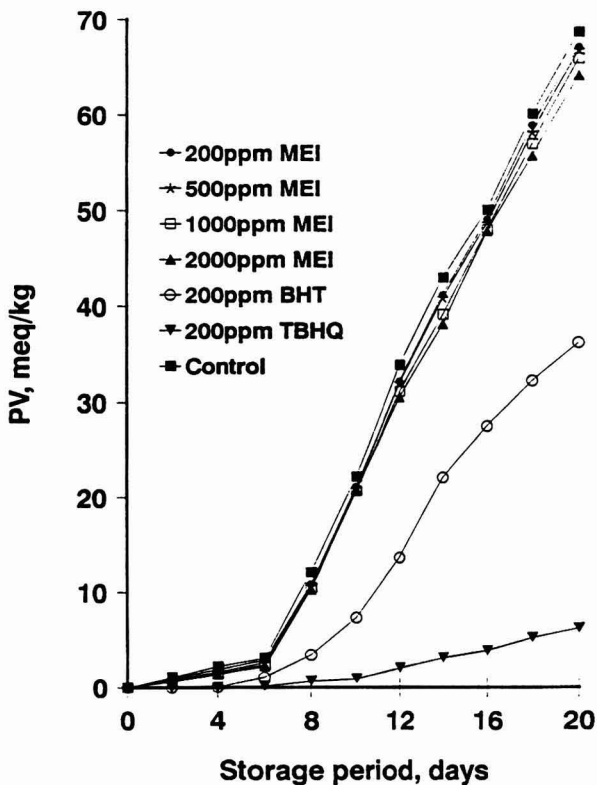
FIG. 6. PEROXIDE VALUE (PV) OF SOYBEAN OIL WITH ADDED METHANOLIC
EXTRACTS OF ISUBGOL (MEI), BHT AND TBHQ DURING STORAGE AT 60C

Heating Tests. The number of 10-h heating cycles was plotted against averaged conjugated diene (CD) values for heating at 180C with addition of MEI (Fig. 7). The data showed a typical pattern in the rise of CD for all treatments.
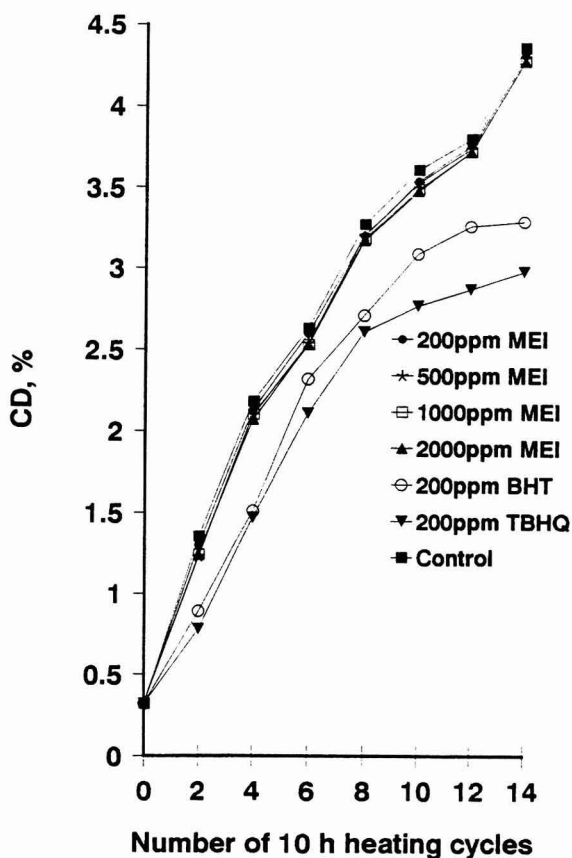
FIG. 7. CONJUGATED DIENE (CD) VALUES OF SOYBEAN OIL
WITH ADDED METHANOLIC EXTRACTS OF ISUBGOL (MEI),
BHT AND TBHQ DURING HEATING AT 180C

During 14 days of heating cycles, the control had the greatest formation of conjugated dienes. The conjugated diene formation values for MEI were not significantly different, except the 0.2% treatment, which indicated the low of antioxidative properties of isubgol.

Fatty Acid Methyl Esters. Fatty acid methyl esters were determined for all treatments of the soybean oils before and after 14 days of heating at 180C (Table 1). The data given are the relative percentages of the each fatty acid present in the soybean oil. Also listed is the 18:2/16:0 ratio, which is a good indicator of heated oil deterioration during heat treatment according to Augustin

TABLE 1.
FATTY ACID METHYL ESTERS OF REFINED, BLEACHED, AND DEODORIZED
SOYBEAN OIL BEFORE AND AFTER 14 DAYS AT 180C

	Fatty acids, %					
Treatment	16:0	18:0	18:1	18:2	18:3	18:2/ 16:0
Day 0 Fresh oil	10.80	3.10	22.50	55.90	7.80	5.18[a]
Day 14 Control	18.50	5.50	33.10	42.90	-	2.30[b]
MEI[1] %,						
0.02	18.30	5.48	33.08	42.89	-	2.34[b]
0.05	18.30	5.46	33.04	42.87	-	2.34[b]
0.1	17.90	5.45	33.00	42.85	-	2.39[b]
0.2	17.90	5.45	33.00	42.85	-	2.39[b]
BHT, 0.02%	16.40	5.30	32.60	46.20	-	2.82[c]
TBHQ, 0.02%	16.10	4.70	29.90	49.20	-	3.06[d]

[1] MEI, Methanolic extracts of isubgol

[a,b,c,d] Means with different letters in the column are significantly different ($P < 0.05$)

et al. (1987). In this study, the ratio 18:2/16:0 was lowest for the control, indicating the greater degree of oil deterioration. The least deteriorated oils were those with TBHQ. However, MEI did not have a ratio significantly different from the control, indicating poor antioxidative properties of the isubgol extracts.

CONCLUSION

Methanolic extracts of isubgol showed poor antioxidative properties in a model system as well as in real lipid system. The ability of MEI to decrease oxidation of linoleic acid in an aqueous medium in the model system was not

significantly different from that of the control, except for TBA values. Storage and heating tests also showed no significantly different stability of soybean oil treated with MEI, and the control. The amount of formation of conjugated dienes, and consequently, the primary and secondary products of oxidation were the same for the control and experimental treatments with MEI, which indicated poor antioxidative properties of isubgol. Thus, isubgol is not a potential source of natural antioxidant.

REFERENCES

ALLEN, J.C., FARAG R.S. and CROOK, E.M. 1979. The metal-catalyzed oxidation of aqueous emulsions of linoleic acid and trilinolein. J. Appl. Biochem. *1*, 1–15.

ALLEN, J.C. and HAMILTON, R.J. 1983. *Rancidity in Foods*, Applied Science Publishers, London and New York.

AOCS. 1987a. Cd 8-53 (86); Peroxide value. In *Official Methods and Recommended Practices of the American Oil Chemists Society*, 3rd Ed., American Oil Chemists Society, Champaign, IL.

AOCS. 1987b. Ti 1a-64 (73); Conjugated diene. In *Official Methods and Recommended Practices of the American Oil Chemists Society*, 3rd Ed., American Oil Chemists Society, Champaign, IL.

AUGUSTIN, M.A., TELINGAI, A. and HENG, L.K. 1987. Relationships between measurements of fat deterioration during heating and frying in RBD olein. J. Am. Oil Chem. Soc. *64*, 1670.

BURTON, G.W. and INGOD, K.U. 1984. Beta carotene: An unusual type of lipid antioxidant. Science. *224*, 569–573.

CHANG, S.S., OSTERIC-MATIJASEVIC, B., HSIEH, O.A.L. and HUANG, C. 1977. Natural antioxidants from rosemary and sage. J. Food Sci. *42*, 1102–1106.

DANIELS, D.G.H. and MARTIN, H.F. 1967. Antioxidants in oats: monoesters of caffeic and ferulic acid. J. Sci. Food Agric. *18*, 589–595.

DUVE, K.J. and WHITE, P.J. 1991. Extraction and identification of antioxidants in oats. J.A.O.C.S. *68*, 365–370.

ERIKSSON, C.F. 1982. Lipid oxidation catalysts and inhibitors in raw materials and processed foods. Food Chem. *9*, 3–19.

FARAG, R.S., BADEI, A.Z.M.A., HEWEDI, F.M. and EL-BAROTY, G.S.A. 1989. Antioxidant activity of spice essential oils on linoleic acid oxidation in aqueous media. J.A.O.C.S. *66*, 792–799.

KEULS, M. 1952. The use of the studentized range in connection with the analysis of variance. Euphytica *1*, 112–122.

LEE, Y.B., KIM, Y.S. and ASHMORE, C.R. 1986. Antioxidant property in ginger rhizome and its application to meat products. J. Food Sci. *51*, 20–23.

MARCO, G.J. 1968. A rapid method for evaluation of antioxidants. J.A.O.C.S. *45*, 594–598.

NEWMAN, D. 1939. The distribution of the range in samples from a normal population in terms of an independent estimate of standard deviation. Biometrika *31*, 20–30.

POKORNY, J. 1981. Stabilization of fats by phenolic antioxidants. Can. Inst. Food Technol. J. *4*, 68–75.

PRATT, D.E. and MILLER E.E. 1984. A flavonoid antioxidant in Spanish peanuts. J.A.O.C.S. *61*, 1064–1067.

RONALD, S.K. and RONALD, S. (ed.). 1991. *Pearson's Composition and Analysis of Foods*, 9th Ed., pp. 642–643, Longman Scientific & Technical, England.

SAS. 1985. SAS User's Guide: Statistics, SAS Institute, Cary, NC.

SHAI, B., JOSEPHSON, D.B. and MAURER, A.J. 1985. Antioxidant properties of rosemary olcoresin in turkey sausage. J. Food Sci. *50*, 1356–1359.

SLOVER, T. and LANZA E. 1979. Quantitative analysis of food fatty acids by capillary gas chromatography. J.A.O.C.S. *56*, 933–943.

STEEL, R.G.D. and TORRIE, J.H. 1980. *Principles and Procedures of Statistics*, 2nd Ed., McGraw-Hill Book Co., New York.

TAGA, M.S., MILLER E.E. and PRATT, D.E. 1984. Chia seeds as a source of natural lipid antioxidants. J.A.O.C.S. *61*, 928–931.

UTILIZATION OF PROTEINS FROM FISHBALL PROCESSING WASHWATER IN FISH CRACKERS ('KEROPOK')

YU SWEE YEAN[1], YEOH KAH CHAI and TERUSHIGE MOTOHIRO

Faculty of Food Science and Biotechnology
Universiti Pertanian Malaysia
43400 UPM Serdang, Selangor, Malaysia

ABSTRACT

Proteins recovered from the washwater of fishball processing were used in fish crackers. Up to 10% of washwater proteins was acceptable to taste panelists. Although appearance, color and crispiness were not affected, flavor scores declined significantly when 20% and above washwater proteins were used. This was also reflected in the scores for overall acceptability. Fish crackers with 10% washwater proteins contain more protein and less fat.

INTRODUCTION

In processing surimi, approximately 30–40% of the protein is lost in washing operations (Pedersen *et al.* 1990). Washing not only removes fat, suspended solids and other water-soluble substances (sarcoplasmic proteins), but more importantly, concentrates the gel-forming myofibrillar proteins (Lee 1984).

Watanabe *et al.* (1982) have estimated that soluble proteins from the first and second stages of the surimi process can be economically recovered. Some methods for recovery of washwater proteins include pH adjustment (Nishioka and Shimizu 1983), heat, complexing agents, electro-coagulation (Hasegawa *et al.* 1982), membrane filtration (Green *et al.* 1984) and air flotation (Beck *et al.* 1974).

In practice however, washwater proteins are normally not recovered for further use and are discharged as wastewater. This is of concern, since the water contains about 3.4 g of protein per liter (Lee 1984), about 80% of which is water soluble. The total protein lost accounts for approximately 30% of the

---

[1]To whom correspondence should be sent.

deboned meat weight (Watanabe *et al.* 1982) and varies from plant to plant, depending upon the amount of water used and the number of washing cycles employed. If this protein could be recovered, product utilization would improve, and in addition, the environmental impact would be reduced.

In Malaysia, there are numerous small factories producing fish jelly products, such as fishballs and fishcakes, using traditional methods. The processing is similar to surimi processing and involves deboning, leaching, mixing, forming and cooking. The major loss of water-soluble proteins occurs after washing in dilute saline, when the excess water is removed by centrifugation. Dehydrators are not used, as these are expensive.

The objective of this research project was, therefore, to recover proteins currently lost in the washwater during fishball processing and to test the acceptability of these proteins by incorporation into fish crackers ('keropok').

MATERIAL AND METHODS

Recovery of Washwater Proteins

Threadfin bream *(Nemipterus tolu)* was purchased fresh from the wholesale market and transported in ice to the laboratory for immediate processing. Proteins from the washwater were recovered from three washing cycles (Fig. 1) by centrifugation at 20,000 × g for 20 min at 5C (Kubota 7800, Kubota Corporation, Tokyo, Japan).

Processing and Evaluation of 'Keropok'

'Keropok' was processed according to Siaw *et al.* (1985). The formulation used was 1:1 fish to flour, 2% salt, 1% sugar and 25–30% water. The mixture was mixed in a bowl mixer (ADE SL18, ADE, Hamburg, Germany) until homogeneous and then stuffed into cellulose casings (35mm diameter, Teepak Shirred TWP, Wienie-Pak Cellulose Casings, Teepak Incorporation, Westchester, lllinois, USA), using a sausage stuffer (Dick, Hamburg, Germany). The stuffed rolls were cooked at 90–95C for 90 min and allowed to cool overnight at 5C. After slicing to a thickness of 2.5–3.0 mm, the samples were dried until a final moisture content of 8–10% was reached. Washwater proteins recovered by centrifugation at 20,000 × g, were used at 0, 5, 10, 20, 30 and 40% as a partial substitute of the fish component. The proportions of the other ingredients used remained unaltered. Linear expansion was measured as in Yu *et al.* (1981)

```
FISH (deheaded and degutted)
    |
    v
Deboning        (6 inch horizontal fishmeat deboner; aperture size:
    |            4mm; Ban Hing Weights and Measures, Kuala Lumpur,
    |            Malaysia)
    v
Fish mince
    |
    |
    v
Washing in 0.2% saline*
    |
    |
    v
Centrifugation ⊕———>    washwater      ———
    |                    proteins               |
    |                    2.56% +                |
    v                                           |
Washing in 0.3% saline*                         |
    |                                           |
    |                                           |
    v                                           |
Centrifugation ⊕———>    washwater      ———      |
    |                    proteins               |
    |                    2.13% +                |
    v                                           |
Washing in 0.3% saline*                         |
    |                                           |
    |                                           |
    v                                           |
Centrifugation ⊕———>    washwater      ———      |
    |                    protein                |
    |                    1.84% +                v
    v
Mixing with other ingredients
    |                              For 'Keropok'
    |                              Processing
    v
Forming into fishballs
    |
    |
    v
Cooking
```
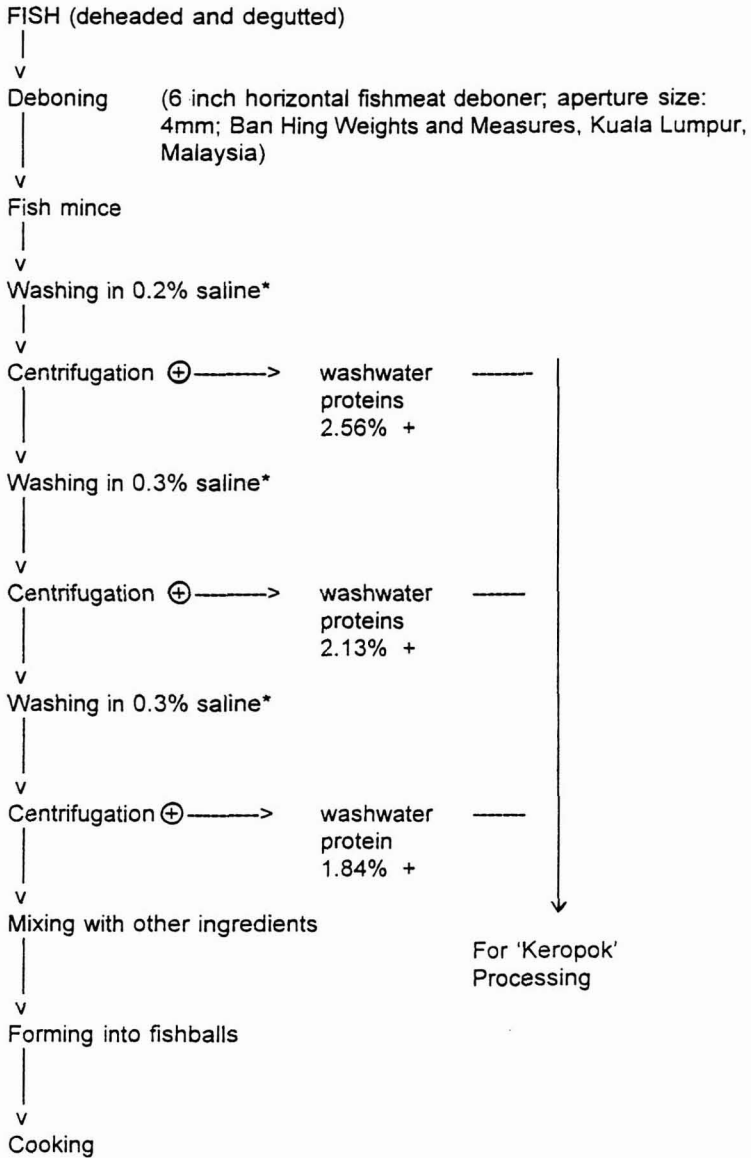
FIG. 1. RECOVERY OF WASHWATER PROTEINS FROM FISHBALL PROCESSING
*5C, 1 fish: 4 saline; + As a percentage of the proteins in the fish mince;
⊕ 20,000 × gravitational force.

after frying in oil at 180C–200C for 30 s. Organoleptic evaluation was done using a taste panel of 20 experienced personnel who were familiar with the product. The panelists evaluated the six samples as shown in Table 1 once. One piece of 'keropok' of each formulation were presented simultaneously to each panelist. The serving order for the six samples was randomized for each panelist. Samples were cooled to room temperature (30C) after frying and evaluated for appearance, color, flavor, crispiness and overall acceptability using a hedonic scale of 9 for excellent and 1 for poor. The acceptance criteria for each attribute was a score of 6 and above (Yu, unpublished observations). Results were analyzed using the analysis of variance (O'Mahony 1986).

TABLE 1.
EFFECT OF WASHWATER PROTEINS ON THE ORGANOLEPTIC PROPERTIES AND
LINEAR EXPANSION OF 'KEROPOK'

| Parameter | % Washwater Proteins | | | | | |
	0	5	10	20	30	40
Appearance	6.25[a]	6.10[a]	6.40[a]	6.00[a]	6.20[a]	6.05[a]
Color	6.90[a]	6.60[a]	7.00[a]	6.75[a]	6.70[a]	6.95[a]
Flavor	7.10[a]	6.95[a]	7.20[a]	5.65[b]	5.10[c]	3.65[d]
Crispiness	7.10[a]	7.15[a]	7.10[a]	7.20[a]	7.05[a]	7.20[a]
Overall* acceptability	6.85[a]	6.70[a]	6.80[a]	5.85[b]	5.70[b]	4.70[c]
% Linear Expansion	90.9	98.4	103.3	101.7	100.0	97.9

1. Means within a column followed by the same letter are not significantly different ($p < 0.05$)

2. *Acceptance for each attribute was a score 6 and above

Chemical Analyses

Analyses for moisture, fat, crude protein and ash were carried out according to Pearson (1970).

RESULTS AND DISCUSSION

Recovery of Proteins from the Washwater

The recovery of proteins from the 3 washing cycles totaled 6.53% of the protein in the first mince (Fig. 1). The recovery rates were lower than those for surimi processing (Watanabe *et al.* 1982; Pedersen *et al.* 1990) as only suspended solids were recovered from the washing processes.

Sensory Evaluation

Results (Table 1) showed that fish crackers containing up to 10% washwater protein were acceptable to taste panelists. Appearance, color and crispiness were unaffected up to 40% protein substitution. Linear expansion for all samples was above the minimum acceptable level of 77% (Siaw *et al.* 1985).

TABLE 2.
PROXIMATE COMPOSITION OF 'KEROPOK' CONTAINING WASHWATER PROTEIN
(BEFORE AND AFTER FRYING)

Parameter	% Washwater Protein					
	0	5	10	20	30	40
Moisture	3.3^a	3.4^a	3.2^a	4.4^b	4.0^b	4.2^b
	(8.9)	(9.6)	(9.2)	(10.1)	(10.2)	(10.0)
Crude protein	13.5^a	14.2^a	16.2^b	16.8^b	18.3^c	19.5^c
	(15.7)	(16.5)	(18.7)	(19.5)	(21.2)	(22.6)
Fat	30.3^a	29.4^a	27.1^a	21.2^b	20.6^b	21.0^b
	(1.10)	(1.06)	(0.74)	(0.65)	(0.53)	(0.35)
Ash	3.43^a	3.42^a	3.21^a	3.31^a	3.31^a	3.21^a
	(4.27)	(4.27)	(4.09)	(4.21)	(4.20)	(3.93)

1. Means within a row followed by the same letter are not significantly different (p<0.05)

2. Figures in brackets are for samples before frying

TABLE 3.
PROXIMATE COMPOSITION OF *NEMIPTERUS TOLU*

Parameter	%
Moisture	78.7
Protein	18.8
Fat	0.9
Ash	1.7

However, flavor was adversely affected. It was observed that samples with higher washwater protein contents tended to absorb less fat upon frying (Table 2). A significant decrease in fat content in samples containing 20% washwater protein after frying (Table 2) coincided with simultaneous significant drops in flavor and overall acceptability scores (Table 1). 'Keropok' is consummed as a fried product and a certain threshold value of fat may be necessary for the correct mouthfeel. This will form the subject of further studies.

ACKNOWLEDGMENT

REFERENCES

BECK, E.L., GIANNINI, A.P. and RAMIREZ, E.R. 1974. Electrocoagulation clarifies food wastewater. Food Technol. *28*, 18–24.

GREEN, D.P., TZOU, L., CHAO, A.C. and LANIER, T.C. 1984. Strategies for handling soluble wastes generated in minced fish (surimi) production. Proc. 39th Ann. Purdue Industrial Waste Conf., Purdue University. pp. 562–572.

HASEGAWA, H., WATANABE, H. and TAKAI, R.1982. Methods of recovery of fish muscle water-soluble protein by electrocoagulation. Bull. Jap. Soc. Sci. Fish. *50*, 659–663.

LEE, C.M. 1984. Surimi process technology. Food Technol. *38*, 69–80.

NISHIOKA, F. and SHIMIZU, Y.1983. Recovery of proteins from washings of minced fish meat by pH shifting methods. Bull. Jap. Soc. Sci. Fish. *49*, 795–800.

O'MAHONY, M. 1986. Sensory evaluation of food. Statistical Methods and Procedures, Marcel Dekker, New York.

PEARSON, D. 1970. *The Chemical Analysis of Foods*, 6th Ed. Churchill-Livingstone, London.

PEDERSEN, L.D., ROSE, W.W., DENISTON, M.F. and MERLO, C.A. 1990. Hyperfiltration Technology for Recovery and Utilization of Protein Materials in Surimi Process Waters. National Food Processors Association, Washington, D.C.

SIAW, C.L., IDRUS, A.Z. and YU, S.Y. 1985. Intermediate Technology for fish cracker ('keropok') production. J. Food Technol. *21*, 17–21.

WATANABE, H., TAKAI, R., SEKIGAWA, A. and HASEGAWA, H. 1982. An estimation of the amount of protein lost in the effluent from frozen surimi manufacture. Bull. Jap. Soc. Sci. Fish. *48*, 869–871.

YU, S.Y., MITCHELL, J.R. and ABDULLAH, A. 1981. Production and acceptability testing of fish crackers ('keropok') produced by the extrusion method. J. Food Technol. *16*, 51–58.

VISCOSITY AND HEAT TRANSFER COEFFICIENTS FOR CANOLA, CORN, PALM, AND SOYBEAN OIL

K.S. MILLER, R.P. SINGH[1] and B.E. FARKAS

Department of Biological and Agricultural Engineering
University of California
Davis, CA 95616

ABSTRACT

To understand the influence of frying oil's physical properties on heat transfer, heat transfer coefficient and oil viscosity were measured for combinations of oil type, temperature, and condition. The lumped capacity method for heat transfer in a high thermally conductive metal gave convective heat transfer coefficients. A capillary viscometer in a convective air heater provided viscosity data at frying temperatures. Frying time and oil temperature significantly affected viscosity. Oil viscosities were not statistically different between fresh and 12 h frying oil or 12 and 24 h frying oil, while between the remaining frying times the oil viscosities were statistically different. Corn oil viscosity showed the greatest increase over 36 h and the highest correlation between viscosity and heat transfer coefficient (−0.959).

INTRODUCTION

Many physical properties of foods vary during frying. Thermal conductivity changes as the crust forms and the food dehydrates. The intrusion of oil into food affects the food's thermal properties, but no single theory as to when oil absorption occurs has been presented in the literature. To further complicate the frying system, the oil's physical and thermal properties also vary.

The literature is replete with papers examining oil quality and stability. Billek *et al.* (1978); and Paradis *et al.* (1981) performed chemical analyses of degraded frying oils. Huang *et al.* (1981), Chang *et al.* (1978), Chu (1991), and Wu and Nawar (1986) have reported physical properties such as oil viscosity, smoke point, and color in addition to the standard chemical analyses for degraded frying oils.

[1]Correspondence to: Dr. R.P. Singh, Department of Biological and Agricultural Engineering, University of California, Davis, CA 95616; (916)752-0811.

461

Stern and Roth (1959) proposed that an oil's physical properties such as viscosity and surface tension could be the primary factors that influence variation in fried food quality as well as change in the heat transfer properties of the frying oil. Recently, Blumenthal and Stier (1991) advanced the "surfactant theory of frying", which hypothesized that quality changes in both frying oil and fried foods resulted from increased concentrations of degradation products in the oil acting as surfactants. However, in both cases no substantiating data were provided.

Ashkenazi *et al.* (1984) examined heat transfer during frying of both a model foam substrate and potatoes and proposed a mathematical model that assumed a constant surface heat transfer coefficient. Dagerskog and Sorenförs (1978) examined the heat transfer in deep fried meat patties at 160C and reported heat transfer coefficients of 500 $\pm$ 200 W/m^{2}C. Hallstrom (1979) studied heat transfer in a meat patty during various frying techniques including deep fat frying and reported surface heat transfer coefficients before water evaporation in the patty of 250–300 W/m^{2}C. Keller and Escher (1989) examined the temperature profile in a potato stick as it fried and proposed energy balances and phase diagrams for the frying process. None of these researchers examined the change in heat transfer coefficient as oil degrades.

Shaw and Lukes (1968) recorded fresh oil viscosity at temperatures up to 205C in an attempt to design a fryer that would produce potato chips of reduced oil content and reported Saybolt viscosities for soybean oil of 47.6 s at 121C, 41.4 s at 149C, 38.2 s at 177C, and 36.1 s at 204C. ASTM (1992) standard designation D2161-87 describes the relationship between kinematic viscosity and Saybolt viscosity. Clements *et al.* (1991) presented experimental viscosity and density data for various vegetable oils in the temperature range from 25C to 140C, and Kubota *et al.* (1982) developed prediction equations for density and viscosity for various vegetable oils in the temperature range from 10C to 60C. No information is available on viscosity values up to 190C for degraded frying oils.

Kress-Rogers *et al.* (1990) tested a sensor that records frying oil viscosity by measuring damping of the vibrations in a piezocrystal, which is a function of the oil's viscosity. The authors contend that "measurement of viscosity promises to be superior to other rapid tests in...independence of oil type and frying conditions...and is a good indicator of oil quality at frying temperatures as well as the lower temperatures employed to date."

Extensive research has been done to describe the chemical changes in frying oils, but few have attempted to relate these chemical changes to the thermal properties of the oil. The goal of this study was to identify the relationships among frying oil viscosity and heat transfer coefficient and to evaluate how these thermal and physical oil properties were affected by oil degradation.

MATERIALS AND METHODS

Oil viscosity was measured at high temperatures using a Cannon™ Ubbelhode calibrated capillary viscometer (size 75, by Cannon Instrument Co., State College, PA) contained in a convective air heater shown in Fig. 1 composed of an insulated steel housing and aluminum ducts.
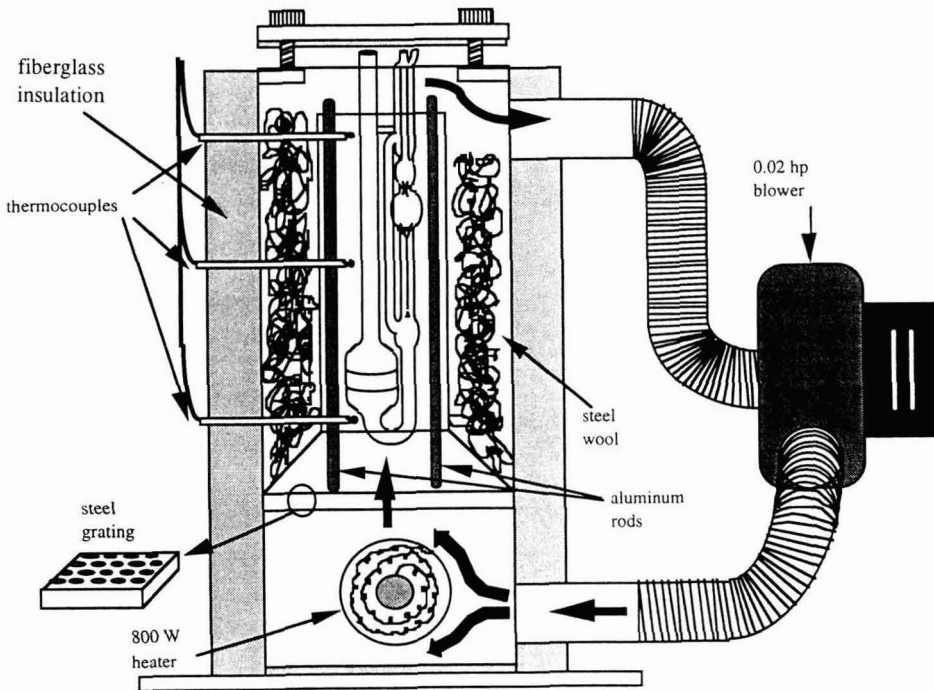

FIG. 1. THE CAPILLARY VISCOMETER WAS KEPT AT CONSTANT HIGH
TEMPERATURES WITH A CONVECTIVE AIR HEATER

The air was heated with a 800 W resistive heater and circulated through an insulated steel housing with a 0.02 hp blower. Data acquisition and temperature control were performed using LABTECH NOTEBOOK™ in a closed loop control configuration with on/off control of the heating element.

Heat transfer coefficients were measured using a lumped capacity analysis (Holman 1990). A spherical aluminum transducer with a stainless steel guide wire attached for support was partially shielded from convective currents due to the heating elements in the oil by an aluminum box. The box had three

thermocouples attached to it so that an average oil temperature could be recorded.

The spherical aluminum transducer (type 1100 alloy aluminum) with diameter 1.22 cm was used to determine the heat transfer coefficient. The density and specific heat for the alloy are $\rho = 2712.64$ kg/m^3 and $Cp = 962.9$ J /kgC (Perry and Green 1984). Heat transfer coefficient measurements were also recorded at three temperatures (170C, 180C, and 190C) for each of the four frying oils at each of the four levels of degradation.

The heat transfer coefficient was calculated from nonlinear regression of the transducer's time-temperature profile (Miller 1992). The BMDPAR™ nonlinear regression routine in the BMDP™ software package (Dixon et al. 1985) fit the time-temperature data to the equation

$$T = T_m + (T_o - T_m)e^{-\left(\frac{3ht}{\rho C_p r}\right)}$$

where T is the transducer temperature in C, T_m is the average oil temperature in C, T_o is the initial transducer temperature in C, t is the time in seconds, ρ is the density of aluminum in kg/m^3, C_p is the specific heat of aluminum in J/kgC, r is the radius of the aluminum transducer in m, and h, the heat transfer coefficient in W/m$_2$C, is the regression variable. A program was written in BMDPAR™, which used nonlinear regression to solve for the heat transfer coefficient for a particular set of transducer time-temperature data.

Canola, corn, soybean, and palm oils were chosen as frying oils that represent a broad spectra of uses in the fried food industry. Several options were suggested in the literature as methods of oil degradation including injecting food grade steam into the frying oil, frying moistened cotton balls, and frying a food product. Frying of Russet potatoes was chosen as the method of degradation for this experiment.

The potatoes were stored at room temperature (approximately 25C) until needed. A frying temperature of 190C was chosen to fry the potato strips. The total degradation time was set as 36 h, and the degradation levels were identified by number of hours the oil was heated during frying. Four degradation levels were chosen and identified as fresh, 12 h, 24 h, and 36 h.

Two hundred grams of Russet potato strips were fried for 5 min at 190C at hourly intervals for a total of 12 h. Fresh potatoes were used at each frying step. Heat transfer measurements were performed promptly after each 12 h interval. The oil was then stored for 36 h in a low temperature incubator (Fisher Scientific, model 307) at 25C while viscosity measurements were taken.

This procedure was repeated twice to provide a total oil degradation time of 36 h for each of the frying oils. Viscosity measurements were recorded using the capillary viscometer at three temperatures (170C, 180C, and 190C) for each of the four frying oils at each of the four levels of degradation. The oil was

filtered with fiber paper of unknown pore size to remove macroscopic particulates before measuring viscosity.

The percent free fatty acid (FFA) was determined by American Oil Chemists' Society method Ca-5a-40 (AOCS 1964). The percent polymer determination was performed using high performance size exclusion chromatography with methods detailed by Christopoulou and Perkins (1986). Oil samples were frozen immediately after collection and shipped in dry ice to Frito-Lay, Inc., Irving, TX. The Analytical Services Department of Frito-Lay, Inc., performed both the percent FFA and the percent polymer analysis for this research using the above methodologies.

RESULTS AND DISCUSSION

The heat transfer coefficient and oil viscosity for corn oil changed the most over the 36 h test as shown in Fig. 2 and Fig. 3. The heat transfer coefficient data and the oil viscosity data for the three remaining oils are given in Table 1. The statistical software package SuperANOVA™ was used to perform the analysis of variance. SuperANOVA™ contains several options for means testing as well as analysis of variance, and one of the most conservative of the means tests (Tukey compromise) was chosen so as to report only the most significance means differences.

The analysis of variance showed that oil viscosity increased with oil degradation time at a 0.1 % significance while decreasing with oil temperature at a 0.1 % significance (Miller 1992). The viscosities among the four oils were not different at a 5% significance. The interaction between oil type and oil temperature had no effect on oil viscosity at a 5% significance (Miller 1992).

Data analysis showed that heat transfer coefficient was not affected by oil degradation time at a 5% significance, but heat transfer coefficient increased with oil temperature at a 0.1% significance (Miller 1992). Neither the oil type nor the interaction between oil type and oil temperature had a significant influence on the heat transfer coefficient at a 5% significance (Miller 1992).

For all four oils, viscosity showed high correlation coefficients, from 0.808 to 0.999, to both percent FFA and percent polymers. However, only corn oil heat transfer coefficient showed high correlation coefficients, from -0.922 to -0.989, to percent FFA and percent polymers. Corn oil viscosity was highly correlated to heat transfer coefficient (-0.959), but for the other three oils no significant correlations existed between viscosity and heat transfer coefficient.

Holman (1990) gives the following empirical correlation for heat transfer coefficient under conditions of free convection

$$Nu = 2 + 0.43 \ (GrPr)^{1/4}$$

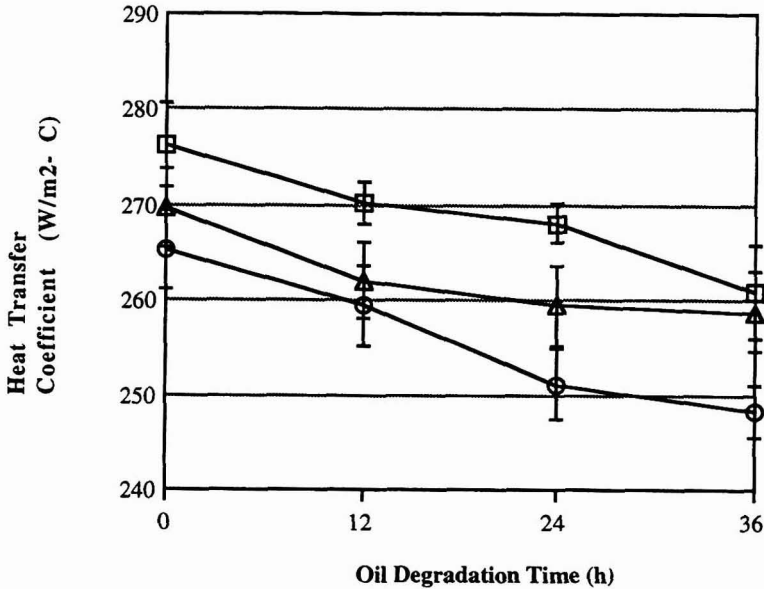where Nu is the Nusselt number, Gr is the Grashof number, and Pr is the Prandtl number.

FIG. 2. HEAT TRANSFER COEFFICIENTS FOR CORN OIL AT 3 TEMPERATURES FOR
4 DEGRADATION TIMES
Error bars show plus or minus one standard deviation ○, 170C, □, 180C, Δ, 190C.

The empirical relation described above for the Nusselt number is recommended for use in free-convection heat transfer from spheres to air, but "in the absence of more specific information it may also be used for liquids" (Holman 1990). The oil density was calculated at the film temperature using the empirical relationship from Toledo (1991).

The film temperature was calculated as the average between the bulk oil temperature and the sphere temperature (where the lumped capacity analysis states that the temperature is assumed to be uniform through out the sphere). The heat capacity for soybean oil at 209C was found in Formo (1979). The thermal conductivity for vegetable oils at 4–187C was taken from Singh and Heldman (1993).

For initial sphere temperatures of 20C, and an oil temperature of 180C Holman's correlation predicted a heat transfer coefficient of 281 W/m²C (Miller 1992). This predicted heat transfer coefficient is very close to the measured values. From these data it would appear that Holman's correlation can be used to estimate heat transfer coefficient for free convection between a sphere in oil.
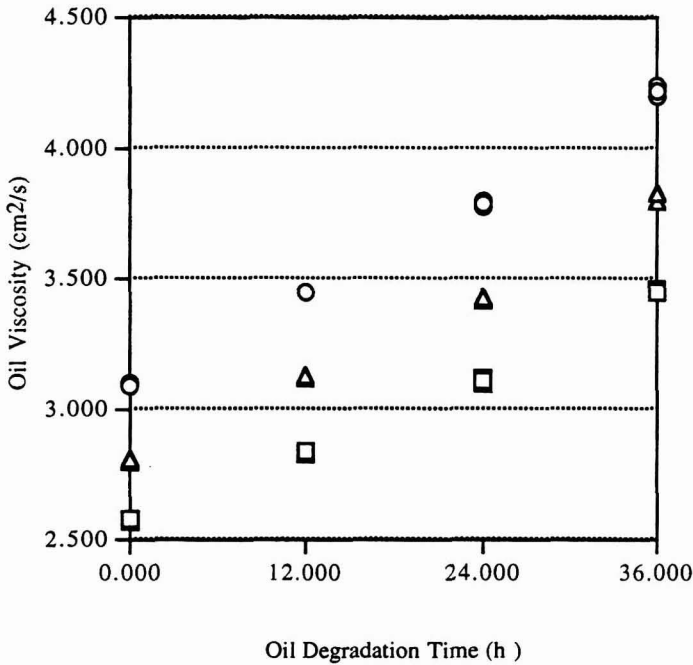
FIG. 3. CORN OIL VISCOSITY AT 3 TEMPERATURES FOR 4 DEGRADATION TIMES
○, 170C, □, 180C, △, 190C.

It is important to remember that the heat transfer examined in this study is from the spherical transducer to the oil. This situation could exist at the beginning stages of frying before the formation of vapor bubbles from the food; but once the food's moisture begins to vaporize off, boiling boundary conditions around the food result in a reduced resistance to heat transfer. The heat transfer coefficients obtained in this study would also be useful in examining heat transfer from a fryer's heating element to the frying oil.

Chemical analyses were performed on the oil samples for percent FFA and for percent polymers. These results are presented in Table 2. The standard deviations reported are based on previous use of the analytical techniques by Frito-Lay, Inc., as duplicates were not performed. Smith *et al.* (1986) report the upper limit of percent FFA to be 1.0%. None of the oils tested in this experiment reached this upper limit of percent FFA. However, the limits of percent polymers were reported by Kress-Rogers *et al.* (1990) to be 10–15%; and each of the four oils tested surpassed the limiting values of 10–15% polymers with corn oil reaching 25.1% polymers.

TABLE 1.
HEAT TRANSFER COEFFICIENTS AND VISCOSITIES FOR CANOLA, PALM, AND SOYBEAN OIL

Temperature C	Degradation Time (sec)	Viscosity (cm²/s)			Heat Transfer Coefficient (W/m C)		
		Canola	Soybean	Palm	Canola	Soybean	Palm
170	Fresh	3.203	3.151	3.029	251.4	261.3	249.5
	12	3.234	3.325	3.295	259.3	253.0	256.0
	24	3.323	3.575	3.609	254.7	267.3	254.6
	36	3.453	3.801	3.944	250.7	249.9	247.8
180	Fresh	2.883	2.880	2.756	265.9	269.7	261.0
	12	2.965	3.040	3.049	271.1	258.5	256.9
	24	3.012	3.191	3.254	262.5	265.7	256.1
	36	3.143	3.429	3.598	268.7	260.8	257.9
190	Fresh	2.606	2.614	2.500	264.4	276.2	271.3
	12	2.705	2.724	2.746	271.1	268.5	268.7
	24	2.746	2.932	2.962	272.2	265.0	275.8
	36	2.870	3.088	3.268	275.4	261.2	259.2

TABLE 2.
PERCENT FREE FATTY ACIDS AND PERCENT POLYMERS FOR FOUR EDIBLE
OILS AT FOUR DEGRADATION TIMES

Oil	Degradation Time (hours)	Percent FFA ($\sigma=0.0043$)	Percent Polymers ($\sigma=0.11$)
canola	fresh	0.03	0.35
canola	12	0.12	2.07
canola	24	0.23	4.79
canola	36	-	-
corn	fresh	0.07	0.39
corn	12	0.16	10.80
corn	24	0.25	18.30
corn	36	0.33	25.10
palm	fresh	0.07	0.78
palm	12	0.17	5.56
palm	24	0.30	16.90
palm	36	0.44	11.80
soybean	fresh	0.03	0.33
soybean	12	0.09	7.72
soybean	24	0.15	14.60
soybean	36	0.19	21.50

These data indicate that percent FFA does not always reliably indicate oil quality. The oils in this experiment were severely degraded by the intermittent frying of potato samples to the point that some contained almost twice the acceptable level of percent polymers. However, none of the oils would be discarded if their quality was judged by percent FFA alone.

The large percentage of polymers present in the 36 h degraded oils (up to 25% for corn oil) is very significant in the context of the surfactant theory of frying presented by Blumenthal and Stier (1991). Polymers can be either polar or nonpolar, and those polymers that are polar fall into the classification of surfactant (Nawar 1985). The results that percent polymers correlate well with heat transfer coefficient in corn oil tend to support the surfactant theory of frying. The influence of oil temperature on viscosity within the range of 170-190C was found to be insignificant at the 5% level (Miller 1992).

Several main conclusions may be drawn from this experiment. Oil degradation time was shown to significantly affect oil viscosity. As the oil degrades, compounds such as long-chained polymers produced by thermal degradation or polar compounds produced by oxidative and hydrolytic degradation are produced, which increases the viscosity of the oil. Heat transfer coefficient was not significantly affected by oil degradation. Despite the high levels of polymers present in the degraded oils (25.1% polymers for 36 h corn oil) the heat transfer coefficients among the four degradation times were not

significantly different for any of the four oils. Heat transfer coefficient showed the greatest correlation to viscosity (-0.96) in corn oil, which had the greatest change in viscosity ($30-35\%$). This indicates that oil must undergo significant physical change before the change in heat transfer coefficient is reflected by viscosity change.

ACKNOWLEDGMENTS

REFERENCES

AOCS. 1964. *Official and Tentative Methods of the American Oil Chemists' Society.*, Vol. 1, 3rd Ed. Amer. Oil Chemists' Soc., Champaign, IL.

ASHKENAZI, N., MIZRAHI, Sh. and BERK, Z. 1984. Heat and mass transfer in frying. In *Engineering and Food*, Vol. 1. (B.M. McKenna, ed.), Elsevier Applied Science Publishers, New York.

ASTM. 1992. Standard practice for conversion of kinematic viscosity to Saybolt Universal viscosity or to Saybolt Furol viscosity, designation D 2161-87. In *Annual Book of ASTM Standards, Sec. 5, Petroleum Products, Lubricants, and Fossil Fuels*, Vol. 5.01, Amer. Soc. of Testing Methods, Philadelphia.

ASTM. 1992. Standard test method for kinematic viscosity of transparent and opaque liquids, designation D 445-88. In *Annual Book of ASTM Standards, Sec. 5, Petroleum Products, Lubricants, and Fossil Fuels*, Vol. 5.01, Amer. Soc. of Testing Methods, Philadelphia.

BILLEK, G., GUHR, G. and WAIBEL, J. 1978. Quality assessment of used frying fats: A comparison of four methods. J. Amer. Oil Chem. Soc. *55*, 728-733.

BLUMENTHAL, M.M. and STIER, R.F. 1991. Optimization of deep-fat frying operations. Trends Food Sci. Technol., June.

CHANG, S.S., PETERSON, R.J., and HO, C.-T. 1978. Chemical reactions involved in the deep-fat frying of foods. J. Amer. Oil Chem. Soc. *55*, 718-727.

CHRISTOPOULOU, C.N. and PERKINS, E.G. 1986. High performance size exclusion chromatography of fatty acids, mono-, di-, and triglyceride mixtures. J. Amer. Oil Chem. Soc. *63*, 679–684.

CHU, Y.-H. 1991. A comparative study of analytic methods for evaluation of soybean oil quality. J. Amer. Oil Chem. Soc. *68*, 379–384.

CLEMENTS, L.D., SHAFER, R., NOUREDDINI, H. and MAMMEL, W. 1991. Density and viscosity for vegetable oils and fatty acids. Paper no. 916522, presented at Dec. 17–20, 1991 International Winter Meeting of the American Society of Agricultural Engineers, Chicago, IL.

DAGERSKOG, M. and SORENFORS, P. 1978. A comparison between four different methods of frying meat patties: Heat transfer, yield, and crust formation. Lebensm. Wiss. Technol. *11*, 306–311.

DIXON, W.J. BROWN, M.B., ENGELMAN, L., FRANE, J.W., HILL, M.A., JENNRICH, R.I. and TOPOREK, J.D. (eds.). 1985. *BMDP Statistical Software: 1985 Printing*, University of California Press, Berkeley, CA.

FORMO, M.W. 1979. Physical properties of fats and fatty acids. In *Bailey's Industrial Oil and Fat Products*, Vol. 1, (D. Swern, ed.). John Wiley & Sons, New York.

HALLSTROM, B. 1979. Heat and mass transfer in industrial cooking. In *Food Process Engineering*, Vol. 1: *Food Processing Systems*, (P. Linko, Y. Malkki, J. Olkku, and J. Larinkari, eds.), Applied Science Publishers, London.

HOLMAN, J.P. 1990. Unsteady state heat conduction. In *Heat Transfer*, 6th Ed., pp. 131–206, McGraw-Hill Book Co., New York.

HUANG, A.-S., HSIEH, O.A.-L., HUANG, C.L., and CHANG, S.S. 1981. A comparison of the stability of sunflower oil and corn oil. J. Amer. Oil Chem. Soc. *58*, 997–1001.

KELLER, C. and ESCHER, F. 1989. Heat and mass transfer during deep fat frying of potato products. Poster presented at International Congress on Engineering and Food, Cologne, Germany, May 5–June 1.

KRESS-ROGERS, E., GILLAT, P.N., and ROSSELL, J.B. 1990. Development and evaluation of a novel sensor for the *in situ* assessment of frying oil quality. Food Contr., July, 163–178.

KUBOTA, K., KURISU, S., SUZUKI, K., MATSUMOTO, T. and HOSAKA, H. 1982. Study on the viscosity and density equations respected (sic) temperature of vegetable oils and salad and frying oils. Nippon Shokuhin Kogyo Gakkaishi *29*, 195–201.

MILLER, K.S. 1992. Physical and thermal properties of edible frying oils. MS thesis, Dept. of Bio. and Ag. Engineering, University of California, Davis.

NAWAR, W.W. 1985. Lipids. In *Food Chemistry*, (O.R. Fennema, ed.). Marcel Dekker, New York.

PARADIS, A.J., and NAWAR, W.W. 1981. Evaluation of new methods for the assessment of used frying oils. J. Food Sci. *46*(2), 449–451.

PERRY, R.H. and GREEN, D. 1984. *Perry's Chemical Engineers' Handbook*, McGraw-Hill Book Co., New York.

SHAW, R. and LUKES, A.C. 1968. Reducing the oil content of potato chips by controlling their temperature after frying. Agricultural Research Service report no. ARS-73-58. U.S. Department of Agriculture, Washington DC.

SINGH, R.P. and HELDMAN, D.R. 1993. Appendix A.2. Physical properties of foods. In *Introduction to Food Engineering*, Academic Press, Orlando, FL.

SMITH, L.M., CLIFFORD, A.J., HAMBLIN, C.L. and CREVELING, R.K. 1986. Changes in physical and chemical properties of shortenings used for commercial deep-fat frying. J. Amer. Oil Chem. Soc. *63*, 1017–1023.

STERN, S. and ROTH, H. 1959. Properties of frying fat related to fat absorption in doughnut frying. Cereal Sci. Today. *4*, 176–179.

TOLEDO, R.T. 1991. Appendix A.8. Basic program for determination of thermal conductivity above and below freezing. In *Fundamentals of Food Process Engineering*, Van Nostrand Reinhold, New York.

WU, P.-F. and NAWAR, W.W. 1986. A technique for monitoring the quality of used frying oils. J. Amer. Oil Chem. Soc. *63*, 1363–1367.

LOW DOSE IRRADIATION OF 'RAINIER' SWEET CHERRIES AS A QUARANTINE TREATMENT

S.R. DRAKE,[1] H.R. MOFFITT[2] and D.E. EAKIN[3]

[1]USDA, ARS, Tree Fruit Research Laboratory
1104 N. Western Avenue, Wenatchee, WA 98801
[2]USDA, ARS
3706 W. Nob Hill Blvd., Yakima, WA 98902
[3]Battelle-Pacific Worthwest Laboratory
P.O. Box 999, Richland, WA 99352

ABSTRACT

'Rainier' cherries, with and without gibberellic acid treatment were subjected to radiation at dose levels of 0.0, 0.1, 0.2, 0.3, 0.4, 0.5, and 1.0 KGy and held for 14 and 21 days at 1C before removal from storage and quality determined. No variation in fruit or stem color, soluble solids, titratable acidity or sensory difference was noted at any of the radiation dose levels. There was 13% loss in firmness due to radiatlon treatment between 0.4 and 1.0 KGy. Cherries that were treated with gibberellic acid were superior candidates for radiation treatment. 'Rainier' cherries can be irradiated as soon as quality parameters have reached acceptable levels for commercial harvest.

INTRODUCTION

Export of agricultural commodities to foreign markets is of major interest to the United States. Fumigation of fruit products with methyl bromide (MeBr) to control insect pests, such as the codling moth [*Cydia pomonella L. (Lepdoptera:Torncidae)*] has met with varying degrees of success due to injury of the host fruit. At the present time, regardless of the problems associated with MeBr as a fumigant, it is the only method accepted by most countries that import fruits and vegetables. In the near future MeBr will be banned from use as a fumigant (UNEP 1992). To continue to export agriculture commodities, alternatives to MeBr must be determined.

Radiation is one of the alternatives to MeBr being considered for insect control. Considerable research has been conducted on irradiation of fruits and

vegetables to control insect disinfestation and postharvest losses. Most of the early work was directed toward producing microbe-free products with greater shelf-life. Levels of gamma radiation necessary to sterilize can cause injury to fresh commodities. Maxie *et al.* (1971) reviewed the effects of radiation on a number of fresh commodities and found that the most severe radiation injury is loss of texture. Lu *et al.* (1989) found that both texture and starch levels were reduced in sweet potatoes as radiation dose rates were increased beyond 1.0 KGy. Miller (1993) found no quality problems in blueberries when radiation dose levels were 0.75 KGy or less. A promising application for radiation was to disinfest papayas of the Hawaiian fruit fly (van Kooij 1991). However, conventional fumigation with ethylene dibromide was the quarantine treatment of choice until its prohibition by EPA (Burditt 1982).

More recent research (Eakin *et al.* 1985) found that codling moth control can be achieved with a radiation dose of less than 0.25 KGy and dose levels up to 0.60 KGy had no adverse effect on 'Bing' cherry quality. Kader (1986) suggested that sweet cherries could be exposed to radiation at levels sufficient for insect desinfestation (< 1 KGy) with little or no quality loss. Jessup (1990) determined that 75 Gy prevented eclosion of Queensland fruit fly and that quality of 'Bing' and 'Lambert' cherries was not influenced by radiation doses far beyond this level. Damayanti *et al.* (1992) determined that the maximum tolerable dose for pineapples *(Anonos comosus* L.) was approximately 2.5 KGy, but doses in the range of 0.50 to 2.5 KGy in combination with 11–13C storage could be used to reduce postharvest losses. Other commodities such as apples have also been shown to be tolerant to low dose radiation with no loss in quality (Massey and Smock 1964; Olsen *et al.* 1989). Agricultural commodities can be disinfested with low dose radiation with no loss in quality, but tolerance of specific cultivars must be determined. Early work using low dose radiation for fumigation concentrated only on dark, sweet cherries such as 'Bing' and 'Lambert' (Eakin *et al.* 1985; Jessup 1990).

Export of light-colored 'Rainier' cherries has increased in the last few years, and alternative methods of fumigation for this cultivar must be considered. Drake *et al.* (1991) reported that 'Rainier' cherries can be fumigated with MeBr with some loss in quality. In addition, 'Rainier' cherries treated with gibberellic acid (GA) were superior candidates for MeBr fumigation compared to non-GA-treated cherries. Other reports (Drake *et al.* 1978; Proebsting *et al.* 1973) have shown that GA-treated 'Rainier' cherries are firmer and have a brighter yellow color than nontreated cherries. The ability of GA to enhance color may prevent or mask phytotoxicity of the fumigation treatment. This study investigated the impact of low dose gamma radiation on 'Rainier' sweet cherries *(Prunus avium* L.) treated with or without GA.

MATERIALS AND METHODS

'Rainier' cherries were obtained from plots of 3 trees each of GA_3-treated and nontreated fruit located at the Washington State University, IAREC, Prosser, WA. Fruit from individual trees were used as replicates. Trees were sprayed with GA_3 at 20 ppm in early May. Cherries were harvested at minimum commercial maturity and again 10 days later. At harvest, cherries were field-packed into 3-kg boxes with liners. Cherries were held overnight at 1C and transported to the irradiation radiator the following day. All radiation treatments were conducted at Battelle-Pacific Northwest Laboratory, Richland, WA using a gamma beam 650 source containing cobalt-60. Distance from the source was adjusted to provide a dose rate of 8.32 Gy/min and exposure time to give total doses of 0, 0.1, 0.2, 0.3, 0.4, 0.5 and 1.0 KGy. Exposure rate was measured using a commercially available small volume ionization chamber made from air equivalatent plastic. After treatment cherries were transported to Wenatchee, WA, and placed in storage at 1C. At 14 and 21 days after harvest cherries were removed from storage and examined for quality. At each examination time 1 kg of fruit was removed from each treatment (harvest/growth regulator/radiation). One-half (500 g) of fruit were examined immediately and the other 500 g examined after 24 h at ambient temperature.

Quality evaluations consisted of fruit weight loss, objective and subjective color, firmness, soluble solids content, titratable acidity and sensory evaluations. Weight loss of fruit was determined by weighing before and after 24 h at ambient temperature. Objective color of fruit and stems was determined with The Color Machine (Pacific Scientific, Silver Springs, MD) using the Hunter "L", "a", and "b" system and calculated hue values (Hunter and Harold 1987). Subjective color was determined using two laboratory personnel familiar with cherry color grades. Fruit and stems were rated individually on a scale of 1 to 3 (1 =best, 3 =poorest) and the mean values reported. Firmness was determined using the Universal TA-XT2 Texture analyses equipped with a 3-mm probe set at 10 mm/s and a penetration distance, after contact, of 7 mm. Soluble solids content of the fruit was determined by an Abbe-type refractometer with a sucrose scale calibrated at 20°. Acids were titrated to pH 8.2 with 0.1 N NaOH and expressed as the percentage of malic acid. Sensory evaluation using only the 0 and 1.0 KGy-treatment was conducted by individuals familiar with cherry flavor and color. Analysis of variance was determined by (SAS 1985) with GA_3 application as the main plot, harvest time as the sub-plot and irradiation levels, storage and ripening as sub-sub plots. Based on significant F-test, means were separated using the Waller-Duncan test.

RESULTS AND DISCUSSION

Radiation treatments used in this study did not have any obvious external effects on fruit even at the highest (1.0 KGy) dose level. When grade or quality of a fruit product were evaluated no flavor differences were evident between control fruit and fruit treated with 1.0 KGy. No color deterioration or phytotoxicity due to radiation treatment was seen in either fruit or stems (Table 1). Other reports (Drake and Mofffitt 1992; Drake *et al.* 1991; Drake *et al.* 1988) have shown that severe phytotoxicity of both fruit and stem can occur in cherries, pears and apples when fumigated with MeBr.

Under present marketing procedures fruit and stem color greatly influences consumer perception of cherry quality. Hunter color "L" and hue values for 'Rainier' cherries increased greater than one unit as the radiation dose increased, but no visible difference were noted by laboratory personnel when visual fruit color assessment was considered (Table 2). As little as one unit of color difference can be visible to the human eye (Hunter and Harold 1987). Hunter fruit color "a" and "b" values did not change as radiation dose was increased from 0 to 1.0 KGy. No consistent stem color change was seen (Table 1). Visual color assessment of stem condition was constant regardless of radiation treatment and agrees with Hunter color evaluations (Table 2). After 24 h at ambient temperature there was no change in Hunter fruit color values (data not shown). There was a reduction in visual assessment of fruit color after 24 h at ambient temperature, and a distinct loss in Hunter stem color. Loss in stem color during a 24 h ambient storage period was not related to radiation treatment. Stems lost green color and were browner after 24 h at ambient temperature regardless of radiation treatment.

Radiation treatment above 0.4 KGy resulted in a 13% loss of firmness immediately after removal from cold storage (Table 2). This reduction in firmness is similar to reported losses in firmness of cherries when methyl bromide is used as a fumigant (Drake *et al.* 1991). There was no reduction in firmness values when radiation doses were between 0.0 and 0.3 KGy. Ambient temperature storage for 24 h had no apparent influence on fruit firmness regardless of radiation doses. Cherries treated with GA were firmer at all radiation levels 0–1.0 KGy) than non-GA treated fruit (Fig. 1). Soluble solids content, titratable acidity and weight loss during ambient temperature storage were not influenced by radiation treatment. In addition, ambient temperature storage had no apparent influence on either soluble solids or titratable acidity values (Table 2).

Use of GA in the management of cherry trees has resulted in light-colored, firmer and larger 'Rainier' cherries (Proebsting *et al.* 1973; Drake *et al.* 1978). GA-treated fruit in this study were more yellow in color with less red blush, firmer and larger in size tban non-GA-treated fruit (Table 1). Visual color

TABLE 1.
COLOR OF 'RAINIER' CHERRIES BOTH FRUIT AND STEM AS INFLUENCED BY LOW DOSE
RADIATION, GIBBERELLIC ACID APPLICATION, HARVEST DATE AND STORAGE TIME

| | Hunter Color | | | | | | | |
| | Fruit | | | | Stem | | | |
	L	a	b	hue	L	a	b	hue
Radiation (KGy)								
0.0	61.8 NS[y]	14.0 NS	17.9 NS	53.0 NS	43.1 NS	-1.4	10.4 NS	97.9 NS
0.1	62.2	13.6	17.8	53.2	43.0	-1.1	10.3	95.2
0.2	63.6	12.5	18.2	56.2	43.5	-1.7	10.6	99.3
0.3	62.2	13.0	17.8	54.2	44.0	-1.7	10.9	98.6
0.4	63.3	12.9	17.6	54.4	43.4	-1.6	10.5	98.3
0.5	63.3	12.8	17.4	54.2	43.4	-1.3	10.5	96.8
1.0	64.2	12.3	17.9	56.1	42.4	-1.1	9.7	96.1
Gibberellic Acid								
Yes	66.8 a[y]	9.0 b	19.4 a	65.1 a	42.4 b	-1.4 NS	9.5 b	97.8 NS
No	59.1 b	17.0 a	16.2 b	43.9 b	44.1 a	-1.5	11.3 a	97.1
Harvest								
I	62.8 NS	14.4 a	17.7 NS	51.6 b	41.6 b	-0.7 a	11.3 a	92.5 b
II	63.0	11.7 b	17.9	57.4 a	45.0 a	-2.2 b	9.5 b	102.4 a
Storage (days)								
14	62.1 b	12.2 b	16.1 b	53.5 NS	44.9 a	-1.6 NS	8.9 b	99.0 a
21	63.7 a	13.9 a	19.5 a	55.5	41.6 b	-1.3	11.9 a	95.9 b

[y]NS = No significant difference.
[y]Means within pairs not followed by a common letter are significantly different (P ≥ 0.05).
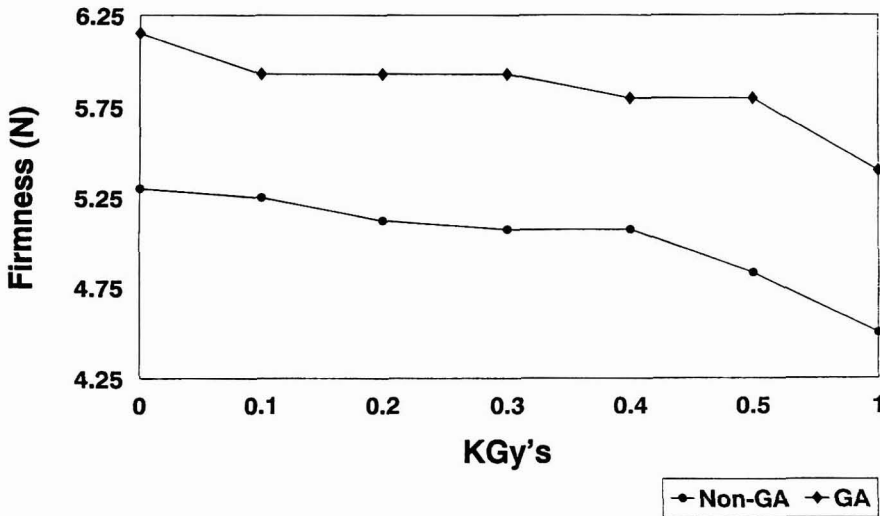
FIG. 1. FIRMNESS VALUES (HARVEST I AND II COMBINED) FOR GA- AND
NON-GA-TREATED 'RAINIER' CHERRIES AS INFLUENCED BY RADIATION LEVEL

assessment agreed with Hunter color results in that GA-treated and nontreated fruit were both rated acceptable in color. These effects on color, firmness and visual assessment were present both immediately after cold storage and after 24 h ambient temperature storage.

Earlier harvested fruit were lighter in color and firmer than later harvested fruit. Tables 1 and 2) both before and after ambient temperature storage. Later-harvested fruit were 21% larger than earlier-harvested fruit (Table 2). Cold storage from 14 to 21 days resulted in some changes in fruit color (Table 1). 'Rainier' cherries were lighter in color (more yellow) after 21 days of storage compared to 14 days of storage. After 24 h at ambient temperature this change in color continued; however, it was more pronounced. Storage had little influence on firmness or size of the fruit.

There was a strong interaction between harvest time and storage on the color of 'Rainier' cherries after 24 h at ambient temperature (Table 3). Early harvested fruit color changed more rapidly due to storage than late harvested fruit. Regardless of storage (14 or 21 days) or ripening time (0 or 24 h) firmness was highest in early harvested fruit compared to later harvested fruit. Fruit weight was not influenced by storage. The largest fruit came from the later harvest with no evidence of quality differences due to storage.

Use of GA helped to maintain the fresh green color of 'Rainier' cherries (Table 1). GA-treated stems were darker in color (lower "a" values) and had

TABLE 2.
QUALITY ATTRIBUTES OF 'RAINIER' CHERRIES AS INFLUENCED BY RADIATION,
GIBBERELLIC ACID, HARVEST DATE AND STORAGE TIME

Radiation (KGy)	Firmness (N)	Soluble solids content (%)	Titratable acidity @ (% malic)	Weight (g)	Visual assessment	
					Fruit	Stems
0.0	5.7 a[y]	19.1 NS[z]	0.45 NS	11.2 NS	1.1 NS	1.3 NS
0.1	5.6 ab	19.3	0.46	11.3	1.4	1.3
0.2	5.5 abc	19.0	0.46	11.2	1.2	1.3
0.3	5.5 abc	19.3	0.46	11.3	1.2	1.3
0.4	5.4 bc	19.5	0.46	11.3	1.1	1.3
0.5	5.3 c	19.4	0.46	11.2	1.1	1.3
1.0	4.8 d	19.3	0.46	11.1	1.1	1.3
Gibberellic acid						
Yes	5.8 a	19.6 a	0.45 NS	12.2 a	1.2 NS	1.3 NS
No	5.0 b	18.9 b	0.47	10.2 b	1.1	1.3
Harvest						
I	5.8 a	19.1 NS	0.48 a	10.0 b	1.1 NS	1.1 b
II	4.6 b	18.9	0.44 b	12.8 a	1.2	1.4 a
Storage (days)						
14	5.1 b	19.0 NS	0.47 a	11.5 NS	1.1 NS	1.1 b
21	5.3 a	18.9	0.45 b	11.3	1.2	1.5 a

[z]NS = No significant difference.
[y]Means within pairs not followed by a common letter are significantly different (P ≥ 0.05).

TABLE 3.
COLOR AND FIRMNESS ATTRIBUTES OF 'RAINIER' CHERRIES AS INFLUENCED
BY THE INTERACTION OF HARVEST DATE AND STORAGE TIME
AFTER 24 H AMBIENT TEMPERATURE STORAGE

Harvest	Storage time (days)	Hunter Fruit Color		Firmness (N)
		L	hue	
1	14	57.5 d[y]	47.5 c	7.1 a
	21	70.4 a	52.5 b	6.2 a
2	14	60.0 c	56.5 ab	4.9 b
	21	65.6 b	57.6 a	5.4 b

[y]Means in a column not followed by a common letter are significantly different (P ≥ 0.05).

higher hue values than nontreated stems. Earlier-harvested fruit had darker green stems immediately after storage or after 24 h at ambient temperature than later-harvested fruit. Additional storage of 14 to 21 days produced darker, less green cherry stems both immediately out of storage and after 24 h ambient temperature storage. The relationship between harvest and storage on stem color was distinct. Hunter "L" values changed more rapidly for earlier harvested fruit from 14 to 21 days of storage, both immediately out of storage and after 24 h ambient temperature storage, than late-harvested fruit. The reverse was true though when hue values were considered and then only immediately after removal from storage.

Eakin *et al.* (1985) reported that on 'Bing' cherries control of codling moth can be achieved with a radiation dose of only 0.25 KGy, and cherry fruit fly can be controlled with a dose of only 0.15 KGy. In this study quality losses were not evident on 'Rainier' cherries with radiation doses up to 0.3 KGy regardless of harvest date. When radiation dose levels increased to 1.0 KGy, the only quality attribute affected was firmness and then a 13% decrease was noted in 'Rainier' cherries. Considering radiation levels necessary for quarantine control (<0.5 KGy) and the lack of quality loss, particularly color, in 'Rainier' cherries with radiation dose levels up to 1.0 KGy, there is little doubt that 'Rainier' cherries are good candidates for fumigation with radiation. Jessup (1990) also found that sweet cherries could be treated with radiation doses sufficient for fumigation, with little loss in quality. Quality loss in radiated sweet cherries is minimal particularly when one considers that more conventional means of fumigation (MeBr) can result in considerable quality loss (Drake *et al.* 1991). Irradiated fruit of superior quality can be placed on the market when cherries are treated with GA before radiation. 'Rainier' cherries should be irradiated as soon as quality parameters reach acceptable levels (color, sugars, acids). A delay in maturity will result in irradiated fruit of reduced quality.

REFERENCES

BURDITT, A.K. 1982. Food irradiation as a quarantine treatment of fruits. Food Technol. *36*, 51–62.

DAMAYANTI, M., SHARMA, G.J. and KUNDU, S.C. 1992. Gamma radiation influences postharvest disease incidence of pineapple fruit. HortScience *27*, 807–808.

DRAKE, S.R. and MOFFITT, H.R. 1992. Winter pear ('Anjou' and 'Bosc') response to methyl bromide fumigation. HortScience *27*, 813–816.

DRAKE, S.R., MOFFITT, H.R, FELLMAN, J.K. and SELL, C.R. 1988. Apple quality as influenced by fumigation with methyl bromide. J. Food Sci. *53*, 1710–1712.

DRAKE, S.R., MOFFITT, G.R. and KUPFERMAN, E.M. 1991. Quality characteristics of 'Bing' and 'Rainier' sweet cherries treated with gibberellic acid, following fumigation with methyl bromide. J. Food Quality *14*, 119–125.

DRAKE, S.R., PROEBSTING JR., E.L., CARTER, G.H. and NELSON, J.W. 1978. Effect of growth regulators on ascorbic acid content, drained weight and color of fresh and processed 'Rainier' cherries. J. Amer. Soc. Hort. Sci. *103*, 162–164.

EAKIN, D.E. *et al.*, 1985. Cherry Irradiation Studies: 1984 Annual Report. Battelle-Pacific Northwest Laboratories, Richland, WA 99352.

HUNTER, R.S. and HAROLD, R.W. 1987. *The Measurement of Appearance*, 2nd Ed., John Wiley & Sons, New York.

JESSUP, A.J. 1990. Gamma irradiation as a quarantine treatment for sweet cherries against Queensland fruit fly. HortScience *25*, 456–458.

KADER, A.A. 1986. Potential application of ionizing radiation in postharvest handling of fresh fruits and vegetables. Food Technol. *40*, 117–121.

LU, J.Y., MILLER, P. and LOCETAN, P.A. 1989. Gamma radiation dose rate and sweet potato quality. J. Food Quality *12*, 369–376.

MASSEY, L.M. and SMOCK, R.M. 1964. Some effects of gamma radiaton on the keeping quality of apples. Agr. Food Chem. *12*, 268–274.

MAXIE, E.C., SOMMER, N.F. and MITCHELL, F.G. 1971. Infeasibility of irradiation fresh fruit and vegetables. HortScience *6*, 202–204.

MILLER, W.R. 1993. Postharvest quality of blueberries irradiated for insect and disease control, pp. 71–76, Proc. 6th Biennial Southeast Blueberry Conf., Feb. 1993, Tifton, GA.

OLSEN, K.L., HUNGATE, F.P., DRAKE, S.R. and EAKIN, D.E. 1989. 'Red Delicious' apple response to low dose radiation. J. Food Quality *12*, 107–113.

PROEBSTING, JR., E.L., CARTER, G.H. and MILLER, H.H. 1973. Quality improvement in canned 'Rainier' cherries (*P. avium* L.) with gibberellic acid. J. Amer. Soc. Hort. Sci. *98*, 334–336.

SAS. 1985. SAS User's Guide, Ver. 5, p. 118, SAS Institute, Cary, NC.

United Nations Environment Programme. 1992. Methyl bromide: Its atmospheric science, technology and economics. U.N. Headquarters, Ozone Secretariat, P.O. Box 300552, Nairobi, Kenya.

VAN KOOIJ, J.G. 1991. International aspects of food irradiation. In *Nutrition Sciences*, Vol. I, (D.A.A. Massel *et al.*, eds.), Food Irradiation Now, Niioff/Junk Publishers.

TEXTURAL CHANGES IN VEGETABLES DURING THERMAL PROCESSING. I. A DESCRIPTIVE METHOD TO SEGREGATE EFFECTS OF PROCESS TREATMENTS

LÍLIA ANDRÉ MOREIRA[1], FERNANDA ADELINA RODRIGUES OLIVEIRA[1,3], JORGE COELHO OLIVEIRA[1] and R. PAUL SINGH[2]

[1]*Escola Superior de Biotecnologia*
Universidade Católica Portuguesa
R. Dr. António Bemardino de Almeida
4200 Porto, Portugal

[2]*Biological and Agricultural Engineering Department*
University of California
Davis, CA 95616-5294, USA

ABSTRACT

Criteria for assessing the effect of processing treatments on the texture of processed foods were developed. Five parameters were defined, relating the hardening or softening of a food material and allowing for the comparison between different processing procedures. In order to determine the usefulness of this method, the parameters were applied to experimental data reported in literature for thermal processing of fruits and vegetables. Three parameters were defined for identifying the effect of a given preprocessing treatment on the raw material texture, the effect of the preprocessing treatment on the sensitivity of the vegetable tissue to the thermal processing and the overall effect. The two remaining parameters were used to describe additional information regarding the process kinetics, that is, to assess the effect of time and temperature on the rate of softening/hardening.

INTRODUCTION

The increasing demand for better quality products from consumers has led to an increasing interest from the processors in developing methods to improve

---

[3]Corresponding author.

the texture of processed vegetables. Texture is one of the most important sensory characteristics of vegetables and perhaps the one most affected by thermal processing.

Preprocessing treatments, such as blanching and addition of calcium chloride, are commonly carried out before vegetable processing (i.e., canning, freezing). Both these pretreatments have been associated with a firming effect and are well-known to improve the texture of the processed product.

It is clear, however, that an adequate development of products with optimum texture depends on the understanding and quantification of the softening process and of the effect of pretreatments on it (Bourne 1989).

Similar to the treatment of chemical reactions, the description of the textural changes due to processing has been attempted using kinetic models, and the textural changes are associated to a time-temperature dependent process. A review of kinetic models used for quantifying the thermal softening of vegetable tissues is given by Bourne (1989). In general, texture of a given sample is characterized by a physical quantity, like the maximum force load obtained from an Instron Universal Testing Machine, and this property is measured as a function of time and temperature. Two models have been generally applied to analyze experimental data: a first order model, where it is assumed that the rate of softening at a fixed temperature is proportional to the property value, the rate will therefore approach zero exponentially; and a two-fraction model, where it is assumed that the vegetable tissue has two fractions, each with its own kinetic parameters, and each following a first order model; for smaller times the fastest process dominates the response, with the fraction associated to it rapidly approaching zero, and for longer times the slowest kinetic process is the fraction observed. In the limiting case of the second fraction with its kinetics being very slow (its rate constant approaches zero), the two-fraction model becomes equal to a single fraction first order with offset.

The interpretation of experimental data is therefore dependent on the identification of one or two straight lines on a semi-logarithmic graph of the property value versus time, for a given temperature. It would be useful if additional methods could be found to clearly identify if there is one first order process (with or without offset) or two processes taking place. In any model, it is usually assumed that the rate constant varies with temperature according to the Arrhenius law.

It is generally concluded that first order models (with one or two fractions) and the Arrhenius dependence of the rate on temperature can represent many experimental results on texture variations (Huang and Boume 1983; Bourne 1989).

It is important to note that if a given pretreatment is used, there are two effects on texture that should be assessed independently: the effect of the pretreatment on the texture of the raw vegetable (which corresponds to a

different texture before the main processing, depending on the pretreatment used) and the effect that the pretreatment has on the sensitivity of the vegetable tissue to the main processing (which means that the softening/hardening kinetics during processing can be different as a result of the pretreatment). In fact, it is not necessarily true that if a pretreatment improves the texture prior to main processing of a vegetable product, the final texture of the processed product is better: the opposite can be true if the tissue becomes more sensitive to the processing method as a result of the changes caused by the pretreatment. This fact will be explored further in this paper.

The interpretation of experimental results on textural changes in foods with the use of kinetic models has a very important role, but also two important limitations: it is only applied to time-temperature dependency and to time temperature evolution that are fairly simple (i.e., it does not account for discontinuities or changes in the type of behavior; e.g. blanching can have a firming effect due to the activation of the pectinmethyesterase enzyme (PME), leading to a situation where a maximum may exist). Thus, there is a need for methods, that complement kinetic analysis, particularly for interpreting and comparing results when certain complex changes in food texture occur.

The objective of this work was the development of a new method to quantify textural changes due to pretreatments and processing steps that would follow an integrated approach and allow to distinguish between the effect of a pretreatment on the texture of the raw product and on the sensitivity of the vegetable tissue to the processing conditions in such a way that the combination of both would also describe total changes in texture. Furthermore, it was intended to analyze the time and time-temperature dependency of a given process without requiring that a model is established *a priori*.

MATERIALS AND METHODS

In order to achieve the proposed objectives, five parameters were defined. These parameters are summarized in Table 1. The definitions are proposed in terms of the different values of the textural property (which can be a firmness reading, a load force, an extrusion force, etc., and is usually expressed in Newtons). The first three parameters are logarithms of ratios, which makes them additive. All parameters can have positive or negative values, with zero meaning that there is no effect, positive values indicating hardening/ less softness and negative values correspond to softening/ less hardness. The values of these parameters for a first order kinetic model are also shown.

Figure 1 shows the relationship between the processing sequences and the nomenclature used for the texture property. As a result of a given process, the

TABLE 1.

SUMMARY DESCRIPTION OF THE PARAMETERS

Parameter	Acronym	Definition	Possible Values	Physical Meaning	Value for 1st order kinetics
Pre processing effect on the Initial Texture	PIT	$Ln \dfrac{F_{T0}}{F_{R0}}$	$+\infty$ hardening 0 no effect $-\infty$ softening	Effect of the pre-processing treatment on the texture of the product (compared to the raw product)	$-k_T \Delta t_T$ [1]
Pre processing effect on the texture Variation due to Processing	PVP	$Ln \dfrac{(F_T/F_{T0})}{(F_R/F_{R0})}$	$+\infty$ more hard/less soft 0 no effect $-\infty$ more soft/less hard	Changes in the texture of the pre processed product (compared to the raw product)	$-(k_P - k_R)\Delta t_P$
Total (pre processing + processing) effect on Product Texture	TPT	$Ln \dfrac{F_T}{F_R}$	$+\infty$ hardening 0 no effect $-\infty$ softening	Comparison between the texture of the pre-processed and the raw product after processing (TPT=PIT + PVP)	$-(k_P\Delta t_P - k_T\Delta t_T)$
Time Step Effect on texture	TSE	$\dfrac{Ln\,(F_{t2}/F_{t1})}{(t2-t1)}$	$+\infty$ hardening 0 no effect $-\infty$ softening	Time effect on texture, at constant temperature	k_P, k_T
Time/Temperature Effect on texture	TTE	$\dfrac{Ln\,(F_{T2}/F_{T1})}{(T2-T1)(t2-t1)}$	$+\infty$ more hard/less soft 0 no effect $-\infty$ more soft/less hard	Effect of temperature and time on texture $TTE=\dfrac{TSE\,(T2) - TSE\,(T1)}{T2-T1}$	α (2)

(1) if the same time is considered

(2) if $k_T = k_{T0} + \alpha T$
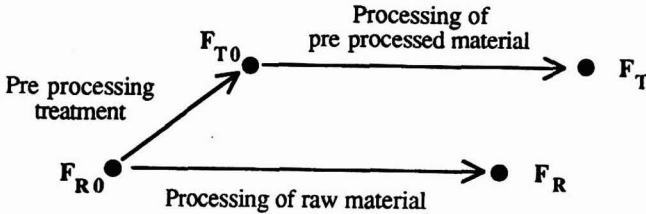
FIG. 1. SCHEMATIC REPRESENTATION OF THE RELATIONSHIP
OF NOMENCLATURE WITH PROCESSING STEPS

texture of a raw vegetable changes from F_{R0} to F_R. As a result of a pretreatment, the texture of a raw vegetable changes from F_{R0} to F_{T0} and a subsequent process causes the texture to change from F_{T0} to F_T. The effect of the pretreatment on the final texture of a product is therefore obtained by comparing F_T with F_R.

The Preprocessing effect on the Initial Texture (PIT parameter) quantifies the softening (if it is negative) or the hardening (if it is positive) of the raw material due to the preprocessing treatment itself.

The PVP (Preprocessing effect on the texture Variation due to Processing) compares the change in texture that occurs during the main processing for a product that was pretreated and the one that would occur if no pretreatment had been used. When this parameter is zero, the pretreatment did not affect the sensitivity of the vegetable tissues to the processing conditions; if it is positive, then less softening (or more hardening) has occurred during processing as a result of the changes promoted by the pretreatment and the reverse, if it is negative.

The Total (preprocessing + processing) effect on Product Texture (TPT parameter) is the mathematical sum of the two previous parameters and quantifies the overall effect on texture. Positive values mean that the final product is less soft than if no pretreatment had been made. The higher this parameter, the more effective the pretreatment was in preventing texture softening.

The Time Step Effect on texture (TSE parameter) evaluates the effect of processing time (at constant temperature). It can be referred to as processing time or preprocessing treatment time. This parameter describes the sensitivity of the product texture to temperature: if a first order model applies, it is simply equal to the rate constant; if a two fraction model is valid, then there will be a set of time intervals at the beginning of the process for which this parameter has a higher value and another at the end of the process for which it has a lower value, with an intermediate region.

The Time Temperature Effect on texture (TTE parameter) combines the effect of time intervals with temperature changes. It can be seen that it is equal to the difference of the TSE parameters at two different temperatures divided by the temperature difference. For a first order rate, it can be determined that if the temperature difference is sufficiently small for the rate constant to have an approximately linear variation with temperature, then the TTE parameter is simply equal to the slope of that linear relationship. Thus, the TTE parameter will increase with temperature, for equal temperature steps, for an Arrhenius law.

The first three parameters quantify the softening caused by the given processing conditions. By comparing against a control sample, it is possible to quantify immediately the effect of a given preprocessing treatment or of changing operating conditions on the final texture. The higher the value of the TPT parameter, the greater the effect. The usefulness of the PVP parameter is to show that a product texture is improved by a given preprocessing treatment, it does not necessarily imply that the final texture of the processed product is better.

The last two parameters are related to the kinetics of the softening process: the effect of time on texture at a given temperature and the combined effect of temperature and time. A processing time/processing temperature that leads to a greater value in the TTE parameter is more beneficial in terms of texture retention.

The best way to visualize the usefulness of these parameters is by applying them to experimental data and to see how conclusions may be drawn easily. Some of the conclusions discussed in the following were left undetected by the original researchers, for lack of an adequate method to analyze and understand the data obtained.

RESULTS AND DISCUSSION

The parameters developed in this paper were tested using data on texture found in literature for processed vegetables. Four sets of experimental data were selected for this work as case studies (Harada *et al.* 1985; Bourne 1987; Canet and Hill 1987; Monsalve-Gonzalez *et al.* 1993).

Case Study I.   Softening During Potato Cooking (Harada *et al.* 1985): Application of the Parameter TSE

Harada *et al.* (1985) studied the softening occurring during the cooking of Bintje Potatoes at 90, 100 and 110C and reported a first order decay at all

temperatures. Figure 2 shows the TSE parameter plotted for the data. It can be seen that softening occurs since all values are negative. It should be noted, however, that if a first order decay would be valid, the TSE parameter would be constant at each temperature. For 100 and 110C, this is approximately the case (with the second time interval giving an odd point), but at 90C, the first two time intervals gave TSE values clearly lower than the other three: this would suggest a two fraction model. In fact, Harada et al. (1985) had reported for potatoes a much lower correlation for this temperature (0.91) than for the others. If a two fraction model is used, the residual (square root of the sum of the squares of the difference between model and experimental points, divided by the number of degrees of freedom) is 0.61, whereas it would be 5.99 for the single fraction reported by Harada et al. (1985). Thus a two fraction model would be more suitable for representing the data at 90C.
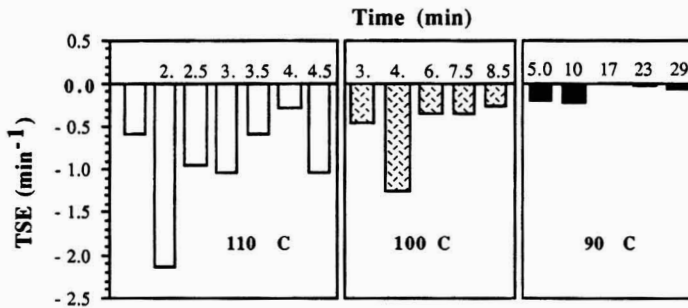
FIG. 2. A COLUMNAR REPRESENTATION OF THE TSE PARAMETER
Calculated from the data of Harada et al. (1985).

Case Study II.   Carrot Softening During Blanching (Bourne 1987): Application of the Parameters TSE, PIT, PVP and TPT

The analysis of rate kinetic data using the TSE parameter is illustrated again with research done by Bourne (1987) on softening of diced Nantes carrots subjected to two different types of blanching and then thermally processed. The TSE values for the two different blanching temperatures are shown in Fig. 3. It can be clearly seen that a single fraction first order model cannot be applied. A two fraction model can be inferred from the first 5 to 6 points, with much lower values (varying around −4.0) and the final 7 to 8 points with values closer to zero. Bourne (1987) had applied the two fraction model to the data, with a good correlation.

Since no standard blanching process is available, the two different blanching conditions may be compared with each other. If a value for a control sample or
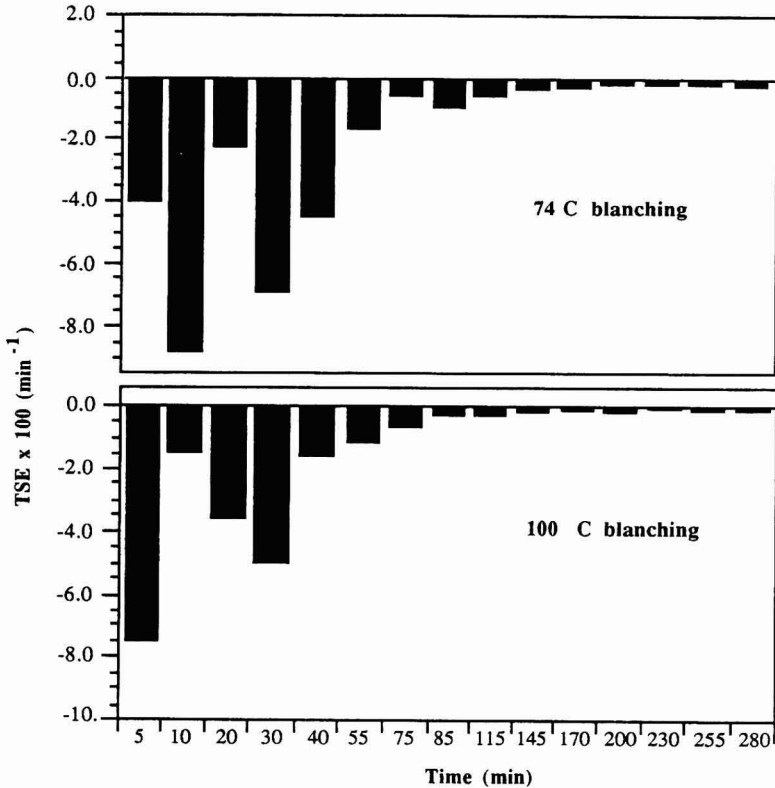
FIG. 3. A COLUMNAR REPRESENTATION OF CHANGE IN THE TSE PARAMETER
Calculated from the data of Bourne (1987).

process did exist, then the PIT value for each blanching condition could be calculated as $\ln(F_{TO}/F_{RO})$ and $\ln(F_{TO}'/F_{RO})$. The difference between the two PIT would be $\ln(F_{TO}'/F_{TO})$. For the PVP and TPT parameters the same procedure can be used. For such a case the parameters are determined taking one as a standard (e.g., blanching at 74C) and calculating the parameters for the other (i.e., each parameter is the difference between the true parameters). The results illustrate the effect of one process compared to the effect of the other. Using this approach the results are the following: PIT = -1.00; PVP = 0.156; TPT = -0.84. These values indicate that the blanching process at 100C led to a softer carrot tissue before the thermal processing (negative PIT) and that although slightly more softening occurred during processing for the carrots blanched at

74C (positive PVP), the final texture is softer for this case (negative TPT: the change caused more softening than the standard).

Case Study III. Effect of Blanching on Cooked Potatoes (Canet and Hill 1987): Application of the Parameters PIT, PVP and TPT

Useful conclusions can be drawn from the data reported by Canet and Hill (1987), most of which were not apparent in the original work. These authors considered thermal processing (cooking) of potatoes, subjected to five different blanching conditions. The different preprocessing treatments are shown in Table 2.

TABLE 2.
THE PREPROCESSING TREATMENTS FOR POTATOES
Used by Canet and Hill (1987).

Reference number	Pre processing treatment
I	Conventional blanching, 97 C, for 2 min
II	Stepwise blanching, 70 C, for 10 min, followed by cooling and then 97 C for 2 min
II	30 s microwave, cooling, then 97 C for 2 min
IV	60 s microwave, cooling, then 97 C for 1.5 min
V	30 s microwave, no cooling, then 97 C for 1.5 min
VI	60 s microwave, no cooling, then 97 C for 1 min

Using the calculated parameters, one can immediately sort the different conditions in terms of their effect on texture before processing, during processing and the total effect. This is shown in Fig. 4. The best final texture is obtained for the preprocessing case identified as number III, since it has the highest TPT, although being negative, which means the potato is softer than the raw potato. It is interesting to note that as a result of the preprocessing using microwaves (numbers III to VI), the potatoes actually harden during the cooking process, thereby compensating for the greater softening that the preprocessing treatment in itself had caused in the raw tissues. The increased hardening during
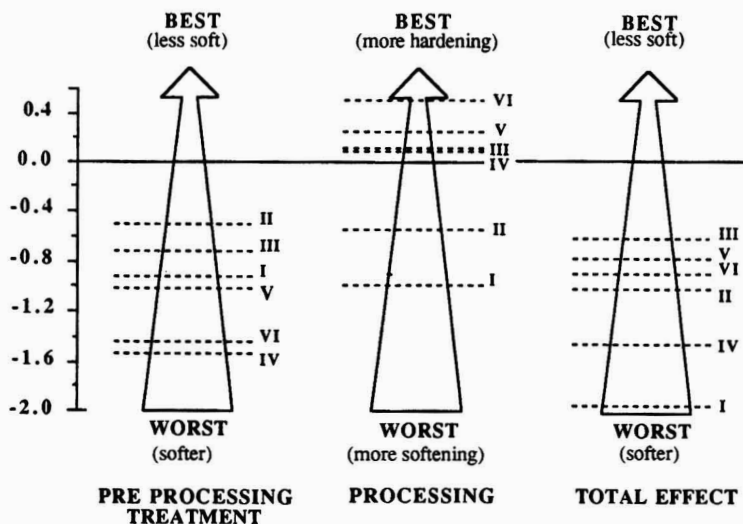
FIG. 4. THE PIT, PVP AND TPT PARAMETERS CALCULATED
From the data of Canet and Hill (1987).

cooking was obtained for preprocessing treatment number VI, but this was not enough to compensate for a too-large softening that occurred in the blanching process. The blanching process that affected the raw potatoes the least was the number II, but since in this case further softening occurred during processing, the final texture was not so good. The use of the above mentioned parameters is particularly useful in situations, such as the one by Canet and Hill (1987). They carried out a cooking process that did not involve a fixed time. The potatoes were cooked until they exhibited the same degree of cooking. Since there are no time-temperature relationships reported, the use of kinetic analysis for interpretation of the data is not possible.

Case Study IV. Osmotic Drying of Apples (Monsalve-Gonzalez et al. 1993): Application of the Parameters TSE and TTE

Monsalve-Gonzalez et al. (1993) studied the osmotic drying of apples in a sugar solution at three different temperatures (30, 40 and 50C). The effect of acidifying with a mixture of citric and ascorbic acids was analyzed. The data reported by Monsalve-Gonzalez et al. (1993) can be used to illustrate the parameters TTE and TSE.

Figure 5 shows the TTE parameters, from which it can be seen that for the nonacidified product, increasing the temperature from 30 to 40C leads to a
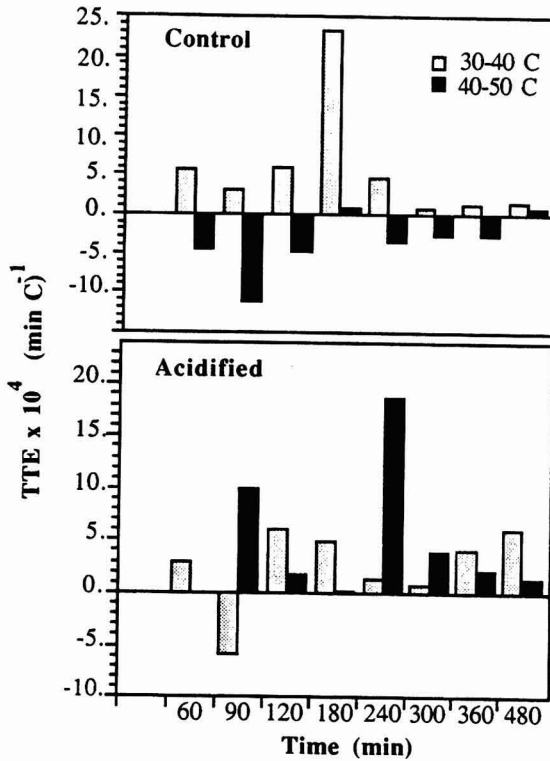
FIG. 5. A COLUMNAR REPRESENTATION OF THE TTE PARAMETER
Calculated from the data of Monsalve-Gonzalez *et al.* (1993).

positive change, since there is less softening, but when the temperature is increased from 40 to 50C, the change is disadvantageous. The best temperature should therefore be 40C. With acidification, however, the increase in temperature is always beneficial, meaning that for acidified samples the best temperature is 50C.

Figure 6 shows the TSE parameter for the data of Monsalve-Gonzalez *et al.* (1993). It can be seen that the softening process cannot be well-described by a single fraction first order model. For the higher times (above 180 min), a first order model may be applied to one fraction of the product, since the TSE parameter is then roughly constant. However, it is evident that an Arrhenius law will not apply for this fraction, since there are many cases, particularly for the nonacidified samples, for which the TSE does not increase with temperature (note that for first order reaction, the TSE parameter is equal to the rate constant k). For shorter time intervals, an increase in the rate constant with time is
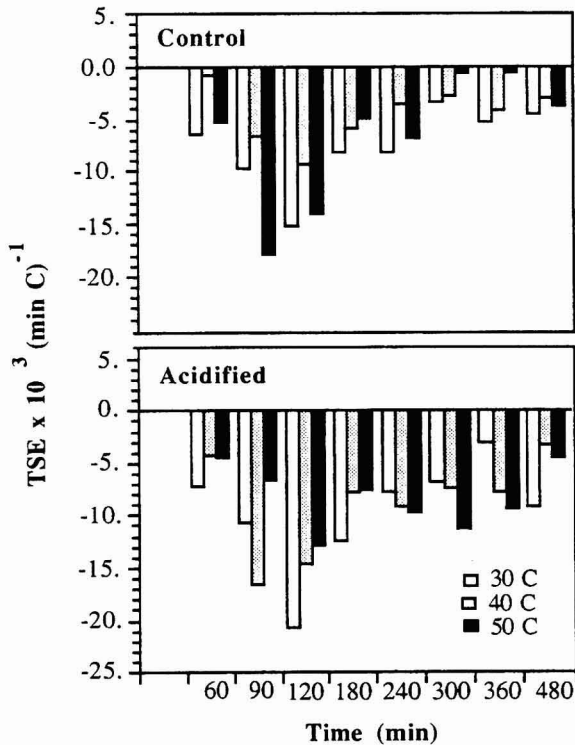
FIG. 6. A COLUMNAR REPRESENTATION OF THE TSE PARAMETER
Calculated from the data of Monsalve-Gonzalez *et al.* (1993)

apparent. This conclusion, however, depends on the certainty of the data, since it depends mostly on the measurements of the second and third point. In this process the variation in texture is very small. Therefore, one is working in a range where differences are of the order of magnitude of experimental errors.

CONCLUSIONS

The five parameters proposed in this paper provide a simple method to analyze data on texture variation due to processing. The parameters are particularly useful when determining the best processing option that maximizes product texture. This approach can be used to complement kinetic modelling, particularly for situations when a simple overall model could not be applied.

NOMENCLATURE

F_R Maximum load force value in the raw product after processing (N)
F_{Ro} Maximum load force value in the raw product before processing (N)
F_T Maximum load force value in the preprocessed product after processing (N)
F_{To} Maximum load force value in the raw product after preprocessing (N)
F_{T1} Maximum load force value in the processed product at temperature T_1 (N)
F_{T2} Maximum load force value in the processed product at temperature T_2 (N)
F_{t1} Maximum load force value in the processed product at time t_1 (N)
F_{t2} Maximum load force value in the processed product at time t_2 (N)
k_P Rate constant for textural changes in the preprocessing, following first order kinetics (s^{-1})
k_R Rate constant for textural changes in the processing of raw product, following first order kinetics (s^{-1})
k_T Rate constant for textural changes in the processing of preprocessed product, following first order kinetics (s^{-1})
k_{T0} Rate constant for textural changes in the processing of preprocessed product, following first order kinetics, at a reference temperature (s^{-1})
T   Temperature (C)
α Slope of the variation of the rate constant with temperature, when a linear dependence can be considered $(C.s^{-1})$
D_{tP} Preprocessing time (s)
D_{tT} Processing time, for both raw and preprocessed product (s)

REFERENCES

BOURNE, M.C. 1983. Physical properties and structure of horticultural crops. In *Physical Properties of Foods*, (M. Peleg and E.B. Bagley, eds.) pp. 207–228, Van Nostrand Reinhold/AVI, New York.

BOURNE, M.C. 1987. Effect of blanch temperature on kinetics of thermal softening of carrots and green beans. J. Food Sci. *52*, 667–668(690).

BOURNE, M.C. 1989. Applications of chemical kinetic theory to the rate of thermal softening of vegetable tissue. In *Quality Factors of Fruits and Vegetables*, (J.J. Jen, ed) pp. 98–139, American Chemical Society, Washington, DC.

CANET, W. and HILL, M.A. 1987. Comparison of several blanching methods on the texture and ascorbic acid content of frozen potatoes. Int. J. of Food Sci. Technol. *22*, 273–277.

HARADA, T., TIRTOHUSODO, H. and PAULUS, K. 1985. Influence of temperature and time on cooking kinetics of potatoes. J. Food Sci. *50*, 459–472.

HUANG, Y.T. and BOURNE, M.C. 1983. Research note: kinetics of thermal softening of vegetables. J. Texture Studies *14*, 1–14.

MONSALVE-GONZALEZ, A., CANOVAS, G.V.B. and CAVALIERI, R.P. 1993. Mass transfer and textural changes during processing of apples by "combined methods". J. Food Sci. *57*, 928–931.

TEXTURAL CHANGES IN VEGETABLES DURING THERMAL PROCESSING. II. EFFECTS OF ACIDIFICATION AND SELECTED PRETREATMENTS ON TEXTURE OF TURNIPS

LÍLIA ANDRÉ MOREIRA[1], FERNANDA ADELINA RODRIGUES OLIVEIRA[1,3], JORGE COELHO OLIVEIRA[1] and R. PAUL SINGH[2]

[1]*Escola Superior de Biotecnologia*
Universidade Católica Portuguesa
R. Dr. António Bernardino de Almeida
4200 Porto, Portugal

[2]*Biological and Agricultural Engineering Department*
University of California
Davis, CA 95616-5294, USA

ABSTRACT

The effect of different preprocessing treatments on the softening of vegetable tissues during acidification of turnips at different temperatures was studied. Texture was characterized by the maximum load force in a puncture test. The different preprocessing treatments considered were blanching alone and coupled with vacuum infusion, freezing/thawing and calcium chloride addition. Samples were acidified at different constant temperatures: 20, 50, 70 and 90C. Results were obtained by comparing the softening occurring for all samples and for non-preprocessed turnips. It was found that for low temperature processing the final result was mainly due to the effect of the preprocessing itself on the turnip texture while for high temperature processing the effect of the preprocessing on the tissues sensitivity to the processing was more important. Blanching alone caused greater softening when processing at 70C but lead to a firmer product when coupled with calcium chloride addition or vacuum infusion for processing at 70 and 90C.

INTRODUCTION

Texture is an important sensory characteristic of vegetables and is an essential property for consumer's perception of quality. Preservation processes

should be designed with a view to ensure a desirable final product texture.

Thermal processing of vegetables is a preservation technique commonly used. In a heating process, during the initial period, the vegetables may actually become firmer, which is an effect associated with enzyme activity. However, as the thermal process proceeds, undesirable softening inevitably occurs. The thermal process itself is determined by the safety requirements. An important objective in the designing a thermal process is to manipulate the process in such a way as to optimize texture, while maintaining safety requirements. Acidification of vegetables can be used with this objective in two ways: lowering the pH below 4.5, decreasing the thermal treatment required (spore forming cells become inactive at that pH and the thermal process needs to ensure only the destruction of less thermal resistant vegetative species); lowering the pH below 3.0, inactivating all bacteria (Jay 1986) — the food is preserved with no thermal process — but acquires a very strong acid flavor. Acidified and thermally processed vegetables have a much better texture than nonacidified ones (Heil and McCarthy 1989; Doesburg 1961). The use of preprocessing treatments has the potential to improve even further the final texture. The purpose of a preprocessing treatment is not only to increase the firmness of the raw vegetable, but also to affect it in such a way that it becomes less sensitive to the softening caused by the thermal process/acidification steps.

Blanching is one of the most important preprocessing treatments in the vegetable processing industry. It leads to the inactivation of enzymes, removal of the air from the vegetables and may also promote the leaching of some undesirable soluble compounds (Lee 1958). Blanching temperatures commonly used (90–100C) may lead to undesirable tissue softening (Bourne 1987).

Sodium chloride and calcium chloride are commonly used in industrial practice as additives. Sodium chloride causes tissue softening (McFeeters *et al.* 1989; McFeeters 1989; vanBuren *et al.* 1988) while calcium chloride may inhibit softening or even increase the firmness (Hughes *et al.* 1975; McFeeters and Fleming, 1989, 1990, 1991; McFeeters 1989). Vacuum infusion removes the air from the vegetable tissue and may be used to infuse compounds into the food with a high mass transfer rate (Javeri *et al.* 1991)

A freezing/thawing process is not in itself a preprocessing treatment, but an inevitable consequence of using frozen vegetables as raw materials. Many food companies use this type of raw material, particularly in some periods of the year when local supply is highly seasonal. Freezing causes a noticeable softening of the vegetable tissue (Brown 1976).

Firmness of vegetable tissues has been widely studied by several authors. Doesburg (1961), Hughes *et al.* (1975), Bourne (1982, 1987), Fuchigami (1987), vanBuren *et al.* (1988), Howard and Buescher (1990), McFeeters and Fleming (1990, 1991) and McFeeters (1992) are examples of studies on firmness measurement in vegetables.

Texture changes are usually associated with a softening process, with a given kinetic model. Hardening is also observed at some conditions (such as blanching at 70C), but in those cases, no kinetic studies have been associated. Texture kinetics are often described using a first order model for low temperatures/short processing times or a double exponential decay model, that assumes the existence of two simultaneous first order softening processes with different rates (Bourne 1987). This last model is used for high temperatures/long processing times (Bourne 1989). Although these models lead to a good description of the experimental results, in some situations they have some drawbacks: they can only be applied to time-temperature dependency and they do not adequately describe complex processes (e.g., when hardening is observed at a given period of the process). For such cases, Moreira *et al.* (1992) have suggested certain parameters that, using an integrated approach, allow for comparison of different processes. These parameters are also useful for assessing the effect of preprocessing treatments and separating the effect of the preprocessing treatment on the texture of the raw product and on the sensitivity of the vegetable tissue to different processing conditions.

The objective of this work was to study the effect of different preprocessing treatments on the softening or hardening processes that occur during acidification of vegetables. In order to obtain a better understanding of the effects, a systematic study was designed, using the same food crop (turnip) for all cases and determining textural changes at different temperatures. Preprocessing treatments studied were blanching, calcium chloride addition, vacuum infusion and freezing/thawing.

MATERIALS AND METHODS

Turnip Samples

Turnips *(Brassica Rapa)* were obtained from the Department of the Portuguese Ministry for Agriculture. Turnips were from the same harvest (January 1992) and stored at 2C and 95% RH for a maximum of one month prior to the experiments.

Before each experiment, the turnips were removed from the storeroom and kept overnight at room temperature. On the following day they were washed, hand peeled and cut in 2.5 cm cubes.

Preprocessing Treatments and Acidification Experiments

The samples were subjected to different procedures, according to the type of effect to be analyzed. These procedures may be divided into 5 types which will be designated by S, B, K, F and V and are summarized in Table 1. Sample C was the control, with no preprocessing. The analysis of the changes caused by preprocessing was done by comparison with the control sample. All the other samples were blanched at 97C for 3 min. After blanching, the samples were cooled by immersion in water (20C, approximately) for 3 min.

TABLE 1.
EXPERIMENTAL PROCEDURE FOR PRE PROCESSING TREATMENTS
AND THERMAL PROCESS

	Pretreatments				Thermal Process
Samples	Blanching (97 C;3min)	Freezing/ thawing	Addition of CaCl$_2$	Vacuum Infusion	Acetic Acid (0.20 $\underline{M}$)
C					X
B	X				X
K	X[1]		X		X[1]
F	X(i)[2]	X(ii)[2]			X
V	X(ii)[2]			X(i)[2]	X

[1] 7% calcium chloride was added both to blanching water and to acetic acid solution
[2] the Romanic numbers indicate the order of execution of treatments

Sample **B** was only blanched. It therefore provided data for the analysis of the effect of blanching alone.

Sample **K** was blanched in a 7% calcium chloride solution, corresponding to calcium addition as preprocessing. In order to prevent calcium chloride from leaching out during the acidification process, the acidification solution used with this sample was an acetic acid solution with 7% calcium chloride.

Sample **F** was blanched and then wrapped in plastic film and frozen overnight in still air at −20C. On the following day, cubes were removed from the freezer and allowed to defrost at room temperature for 6 h and then acidified.

Sample **V** was immersed in a beaker with water and placed in a vacuum oven for 15 min at room temperature and a vacuum pressure of 76 cm Hg and then blanched. Only the cubes that were completely submerged in the water after the vacuum infusion were used for the acidification experiments.

Each turnip sample was acidified in a flask with 50 ml of a 0.2 M acetic acid solution. These flasks were immersed in a thermostatic shaking bath at constant temperature. Before acidification, samples were preheated to the processing temperature to avoid thermal lag effects. More details of the experimental procedure can be found in Moreira et al. (1992). The acidification process was carried out at 20, 50, 70 and 90C. Turnip samples were processed for 220 min, since this was the time necessary for complete acid uptake at any temperature, including 20C (Moreira et al. 1992). In this way, all samples are compared having the same amount of acid. After this processing time, the turnip cubes were carefully removed from the flasks, washed with deionized water, wrapped in aluminum foil and kept in a cold room (10C) until required for further analysis (for a maximum of 6 h).

Firmness

Firmness was measured with an Instron Universal Testing Machine (Model 4501), using a puncture test. The parameter considered for describing firmess was the maximum penetration force, expressed in Newton (Thompson et al. 1982). Measurements were performed at a crosshead speed of 50 mm/min with a 3.2 mm diameter punch and recorded by a data acquisition system linked to the Instron.

Prior to analysis, the samples were removed from the cold room and kept at room temperature ($\approx 25C$) until equilibration. The turnip cubes were then cut in two halves and firmness was measured performing four punches in each half.

RESULTS AND DISCUSSION

Basic Approach

The results are interpreted with the help of four parameters, PIT, PVP, TPT and TTE, previously defined by Moreira et al. (1992). These parameters were applied to assess the influence of blanching, freezing, addition of calcium chloride and vacuum infusion of water on the turnip texture as well as to assess the effect of the simultaneous acidification and thermal process.

Values for these parameters were calculated as the average of 8 different measurements, values and the standard deviation are represented in the following results tables. If the standard deviation is greater than the value itself, then the value is not statistically different from zero and the sample after preprocessing

is not significantly harder or softer than the raw material (control); that is, the preprocessing had no noticeable effect on firmness, measured in terms of a puncture test. To make this situation more evident, values that fell in this case are written in all results tables in italic and underlined. The PVP and TPT parameters are listed in all tables by decreasing order of the parameter: the first value is therefore the one for the option that was least affected by the acidification/thermal treatment at that temperature and the last one is the one that became more sensitive to textural changes during processing. Positive values, that is, samples that did not soften as much as the controls did during the processing, are indicated in bold.

Blanching

Analysis of the results obtained with sample B allows for assessing the effect of blanching alone on the product texture. The PIT parameter for those samples was -0.015 ± 0.076. This means that the blanching process itself did not change significantly the texture of the turnips. The PVP and TPT parameters are shown in Table 2. They are very similar, which would be expected since the PIT parameter approached zero. It is interesting to note that blanching did not affect significantly the final texture, except at 70C, where it caused a more significant softening, due to the fact that the tissues softened more during the processing than they did with the nonblanched controls. This observation can be linked to the activity of the PME enzyme. The blanching treatment was checked with the peroxidase test to be sufficient for enzyme inactivation, and therefore the blanched samples did not have PME activity during the processing. This enzyme activity is present in the control samples, since this enzyme is activated around 70C (McFeeters 1985; Bourne 1987). When processing at this temperature it would be expected that a firming effect would occur during the first few minutes. The final texture would therefore be less soft. When processing at 90C, however, the PME enzyme is quickly inactivated during the processing itself (Belitz and Grosch 1987) and since the processing time is comparatively long, this firming effect is no longer observed.

Other Pretreatments

The individual effects of the other pretreatments may be analyzed by comparison with the ones obtained with the blanched sample (B). As all samples were blanched, a comparison with the control sample would yield the effect of both the blanching and the extra treatments. Given the definition of the parameters, calculating them using Sample B as controls is equal to subtracting

TABLE 2.

PVP AND TPT PARAMETERS FOR BLANCHED SAMPLES

	Temperature (C)			
	20	50	70	90
PVP	-0.0045 ± 0.20^1	-0.15 ± 0.20^1	-0.51 ± 0.19	-0.32 ± 0.41^1
TPT	-0.019 ± 0.21^1	-0.17 ± 0.21^1	-0.53 ± 0.20	-0.34 ± 0.40^1

[1] samples that had the same behavior as the control (in this case the standard deviation is larger than the parameter value)

TABLE 3.

DIFFERENCE BETWEEN THE PIT PARAMETERS OF PRETREATED
SAMPLES AND SAMPLES BLANCHED ONLY

Samples	PIT
K	$+0.037 \pm 0.10^1$
V	-0.081 ± 0.10^1
F	-0.41 ± 0.12

[1] samples that had the same behavior as the blanched only (in this case the standard deviation is larger than the parameter value)

TABLE 4.

DIFFERENCE BETWEEN THE PVP PARAMETERS OF PRETREATED
SAMPLES AND SAMPLES BLANCHED ONLY

Temperature (C)							
20		50		70		90	
(F)	$+0.17 \pm 0.28^2$	(V)	$+0.21 \pm 0.24^2$	(V)	$+0.76 \pm 0.30^1$	(K)	$+2.00 \pm 0.43^1$
(K)	$+0.14 \pm 0.24^2$	(K)	$+0.03 \pm 0.23^2$	(K)	$+0.67 \pm 0.24^1$	(F)	$+1.98 \pm 0.41^1$
(V)	-0.13 ± 0.24^2	(F)	-0.38 ± 0.24	(F)	$+0.18 \pm 0.31^2$	(V)	$+0.89 \pm 0.42^1$

[1] samples that did not soften as much as those blanched only;
[2] samples that had the same behavior as those blanched only (in this case the standard deviation is larger than the parameter value)

the parameters of Sample B from the others. Tables 3, 4 and 5 show the difference between the PIT, PVP and TPT parameters, respectively, for the sample in question and for a blanched sample. From those results it can be seen that freezing was the only preprocessing treatment affecting texture prior to processing, leading to a significant softening. This would be expected, as the texture of vegetables depends mainly on the integrity of cell wall and on turgor pressure. The formation of ice inside the vegetable tissue ruptures the rigid cell wall and the consequent release of intercellular material; when the frozen cells are thawed the water is lost, along with the soluble substances from the ruptured cell and the tissue loses turgor (Brown 1976).

TABLE 5.

DIFFERENCE BETWEEN THE TPT PARAMETERS OF PRETREATED SAMPLES
AND SAMPLES BLANCHED ONLY

Temperature (C)			
20	50	70	90
(K) +0.18±0.26[2]	K) +0.07±0.22[2]	(K) +0.71±0.26[1]	(K) +2.04±0.43[1]
(V) -0.21±0.26[2]	(V) +0.13±0.26[2]	(V) +0.68±0.32[1]	(F) +1.57±0.42[1]
(F) -0.24±0.30[2]	(F) -0.79±0.26	(F) -0.23±0.34[2]	(V) +0.81±0.42[1]

[1] samples that did not soften as much as those blanched only;
[2] samples that had the same behavior as those blanched only (in this case the standard deviation is larger than the parameter value)

Processing at Low and High Temperatures

For processing at low temperatures (20 and 50C) there is almost no difference in the behavior: the softening during processing is similar in all cases and so is the final texture. An exception was observed when processing at 50C, where frozen sample became more sensitive: this means that they soften more than all the others. Adding to the fact that the initial sample was already soft due to the freezing, acidification resulted in a final texture significantly softer than the other ones.

When processed at 70C, vacuum infusion and addition of calcium chloride have a positive effect compared to blanching alone. Furthermore, it can be seen from Tables 2 and 4 that the PVP and TPT parameters of these samples compared to the control are positive. This means that when processing at 70C blanching alone led to a softer final texture but when coupled to either the vacuum infusion or calcium chloride treatments, the result was firmer texture

than with nonpreprocessed samples. At this temperature, the influence of freezing was not significantly different from that of blanching alone.

For processing at 90C, all extra preprocessing treatments were beneficial, compared to blanching alone. Since at this temperature blanched and control samples had the same texture, all these treatments were better than no preprocessing. It is interesting to note that freezing had a positive effect, more beneficial even than vacuum infusion. This is related to the fact that freezing/thawing affects tissues so much that they lose a lot of their sensitivity to temperature. Therefore, at high temperatures these tissues suffer less damage comparatively to their initial condition than others. It is also important to note that vacuum infusion was not so effective for 90C processing than it was for 70C. Although having a positive effect compared to blanching alone, vacuum infusion was less important than addition of calcium chloride and freezing.

Comparing the results in the Tables 3, 4 and 5, it can be seen that for the lower temperatures the results were mainly due to the effect of preprocessing on product texture, while at higher temperatures the effect of the sensitivity of the tissues during processing became more relevant.

The effect of temperature is better analyzed with the TTE parameter, shown in Fig. 1. It can be seen that increasing processing temperature causes a greater softening for the same processing time, although this effect is not so important for freezing and addition of calcium chloride. These two preprocessing treatments decrease the sensitivity of the softening process to temperature. The other preprocessing treatments show a similar behavior for raw tissue.
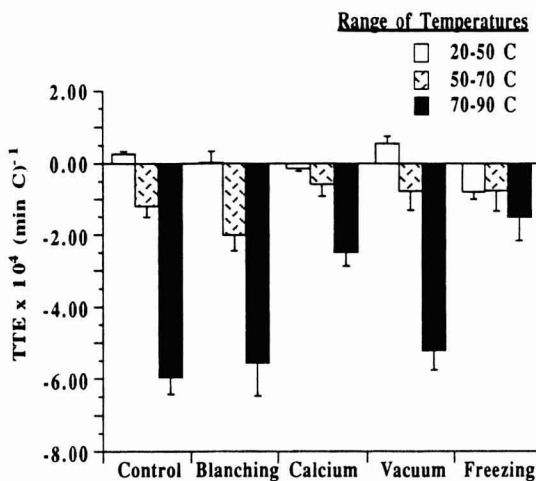
FIG. 1. VALUES OF THE TTE PARAMETER FOR THE DIFFERENT SAMPLES

CONCLUSIONS

At low processing temperatures (20 and 50C) the texture changes were mild; therefore the final product texture was dependent on the influence a given preprocessing treatment had on texture prior to processing. From the preprocessing treatments considered in this study, freezing was the only one that affected product texture, leading to a significant softening.

Blanching showed a negative effect for samples processed at 70C. However, coupling blanching to calcium chloride addition or vacuum infusion led to better results. Vacuum infusion was however less beneficial for processing at 90C. A firmer effect of calcium chloride addition has been found by many authors (Tang and McFeeters 1983; Howard and Buescher 1990; McFeeters and Fleming 1990). It is interesting to note that its effect is twofold: it decreases the softening rate at a given temperature and it also decreases the sensitivity of the softening process to temperature changes. The effect of vacuum infusion has not been studied previously on its own. Vacuum infusion has been used to infuse some additive (e.g., calcium chloride and citrus pectinmethylesterase, Javeri et al. 1991; polyamines, Ponappa et al. 1993), and it is the additive in itself that has the firming effect. In this work, since no additive was used, the air trapped in the interstitial cell space was simply replaced by water and therefore the only effect was the change in cell turgor. This appears to be an interesting process for improving product texture, since it does not involve the use of any chemical.

Freezing/thawing did not lead to significant softening for processing at higher temperatures: at 70C it led to similar results as for samples that were only blanched, and at 90C it even led to a firmer final texture than all other samples, except the ones with calcium chloride addition.

It should be noted that all the above conclusions were obtained for long processing times that obviously led to a considerable texture degradation; although they provide information on extreme effects of the studied preprocessing treatments, they should not be extrapolated for shorter processing times.

ACKNOWLEDGMENTS

REFERENCES

BELITZ, H.D. and GROSCH, W. 1987. *Food Chemistry*, pp. 124–125, Springer-Verlag.

BOURNE, M.C. 1982. Effect of temperature on firmness of raw fruits and vegetables. J. Food Sci. *47*, 440–444.

BOURNE, M.C. 1987. Effect of blanch temperature on kinetics of thermal softening of carrots and green beans. J. Food Sci. *52*, 667–668 (690).

BOURNE, M.C. 1989. Applications of chemical kinetic theory to the rate of thermal softening of vegetable tissue. In *Quality Factors of Fruit and Vegetables Chemistry*, (J.J. Jen, ed.) pp. 98–139, American Chemical Society Symp. Ser., Washington, DC.

BROWN, M.S. 1976. Effects of freezing on fruit and vegetable structure. Food Technol. *30*, 106–114.

DOESBURG, J.J. 1961. Relation between the behavior of pectic substances and changes in firmness of horticultural products during heating. Qual. Plant. Mater. Veg. *VIII*, 115–129.

FUCHIGAMI, M. 1987. Relationship between pectin compositions and the softening of the texture of Japonese Radish roots during cooking. J. Food Sci. *52*, 1317–1320.

HEIL, J.R. and McCARTHY, M.J. 1989. Influence of acidification on texture of canned carrots. J. Food Sci. *54*, 1092–1093.

HOWARD, L. R. and BUESCHER, R. W. 1990. Cell wall characteristics and firmness of fresh pack cucumber pickles affected by pasteurization and calcium chloride. J. Food Biochem. *14*, 31–43.

HUGHES, J. C., FAULKS, R. M. and GRANT, A. 1975. Texture of cooked potatoes: relationship between the compressive strength of cooked potato disks and release of pectic substances. J. Sci. Food Agric. *26*, 731–738.

JAVERI, H., TOLEDO, R. and WICKER, L. 1991. Vacuum infusion of citrus pectinmethylesterase and calcium effects on firmness of peaches. J. Food Sci. *56*, 739–742.

JAY, J. 1986. *Modern Food Microbiology*, Van Nostrand Reinhold Co., New York.

LEE, F.A. 1958. The blanching process. Advan. Food Res. *8*, 63–109.

McFEETERS, R.F. 1985. Changes in pectin and cellulose during processing. In *Chemical Changes in Food During Processing*, (T. Richardson and J.W. Finley, eds), pp. 347–372, Van Nostrand Reinhold/AVI, New York.

McFEETERS, R.F. 1989. Function of metal cations in regulating the texture of acidified vegetables. In *Quality Factors of Fruit and Vegetables Chemistry and Technology*, (J.J. Jen. ed.) pp. 125–139, American Chemical Society Symp. Ser., Washington, DC.

McFEETERS, R.F. 1992. Cell wall monosaccharide changes during softening of brined cucumber mesocarp tissue. J. Food Sci. *57*, 937–953.

McFEETERS, R.F. and FLEMING, H.P. 1989. Inhibition of cucumber tissue softening in acid brines by multivalent cations: Inadequacy of the pectin "Egg Box" model to explain textural effects. J. Agric. Food Chem. *37*, 1053–1059.

McFEETERS, R.F. and FLEMING, H.P. 1990. Effect of calcium ions on the thermodynamics of cucumber tissue softening. J. Food Sci. *55*, 446–448.

McFEETERS, R.F. and FLEMING, H.P. 1991. pH effect on calcium inhibition of softening of cucumber mesocarp tissue. J. Food Sci. *56*, 730–735.

McFEETERS, R.F., SENTER, M.M. and FLEMING, H.P. 1989. Softening effects of monovalent cations in acidified cucumber mesocarp tissue. J. Food Sci. *54*, 366–370.

MOREIRA, L.A., OLIVEIRA, F.A.R. and SILVA, T.R. 1992. Prediction of pH changes in processed acidified turnips. J. Food Sci. *57*, 928–931.

PONAPPA, T., SCREERENS, J.C. and MILLER, A.R. 1993. Vacuum infiltration of polyamines increases firmness of strawberry slices under various storage conditions. J. Food Sci. *58*, 361–364.

TANG, H.-C.L. and McFEETERS, R.F. 1983. Relationships among cell wall constituents, calcium and texture during fermentation and storage. J. Food Sci. *48*, 66–70.

THOMPSON, R.L., FLEMING, H.P., HAMANN, D.D. and MONROE, R.J. 1982. Method for determination of firmness in cucumber slices. J. Texture Studies *13*, 311–324.

VANBUREN, J.P., KEAN, W.P. and WILKISON, M. 1988. Influence of salts and pH on the firmness of cooked snap beans in relation to the properties of pectin. J. Texture Studies *19*, 15–25.

PROTEIN CONCENTRATE FROM CAPELIN
(*MALLOTUS VILLOSUS*) BY SPRAY DRYING PROCESS
AND ITS PROPERTIES

V. VENUGOPAL, A.M. MARTIN[1], S. OMAR and T.R. PATEL

Memorial University of Newfoundland
Department of Biochemistry
St.John's, Newfoundland
Canada A1B 3X9

ABSTRACT

A process is described for preparing protein powder from washed capelin meat. Whole capelin was subjected to mechanical deboning, and the mince obtained was submitted to a three-step washing procedure using cold aqueous solutions of 0.5% NaCl and 0.5% NaHCO$_3$ and, finally, cold water. The washed mince was homogenized in an equal quantity of cold water, heated to 70C to reduce viscosity, and centrifuged at 1160 × g for 15 min to remove traces of sediments. The supernatant, containing more than 90% of the washed mince, was spray dried to obtain a powder with a protein content of 85% and having appreciable functional properties.

INTRODUCTION

The catch of conventional fish species is not keeping pace with the increasing global demand for them. The shortfall, to some extent, could be met by making better use of by-catch and under-utilized species, which form a large share of total marine landings (James 1992; Whittle and Hardy 1992). A plausible approach would be to recover the flesh from these fish species and to further process it into value-added products (Venugopal 1992). One of the processes that received much attention during the sixties and seventies was that for producing fish protein concentrate. However, it failed to reach commercial success due to such problems as high cost of production, poor functional properties of the protein and the presence of residual solvent used for removal

---

[1]Author to whom correspondence should be sent.

of fat in the final product (Finch 1977). A need therefore exists for a viable alternative process to isolate protein from these fish species without significant loss in functionality.

Capelin *(Mallotus villosus)* is a typical low-cost, under-utilized fish abundantly available during summer in countries such as Canada and Norway. In Canada, this fish has limited commercial value. However, in Japan the roe of the female capelin are eaten (Andrews 1988), and in Norway, most of its catch is used for fish meal production (Eide *et al.* 1982). In this paper, a process is reported for the development of spray dried protein powder from capelin. Some of the functional properties of the powder are also presented.

MATERIALS AND METHODS

Fish

Capelin *(M. villosus)*, immediately after landing, were subjected to mechanical deboning using a Baader 694 unit, and the mince was frozen and stored at −20C until used.

Preparation of Dispersion

The frozen fish mince (1 kg) was thawed under running tap water (temperature < 10C) and then subjected to a three-step washing procedure (Venugopal *et al.* 1994). In this, the thawed mince was treated with cold water containing 0.5% NaCl followed by 0.5% NaHCO$_3$ solution and finally with cold water (temperature < 10C). For each treatment (duration, 10 min), the mince was gently stirred in 2 L of the wash medium and then decanted through a sieve (mesh size, 16 mm). After the final wash, the mince was stirred into an equal amount of cold water. The suspension was held overnight at ambient temperature (24–25C), and then homogenized in a blender for 15 s. The homogenate was then heated at 70C for 10 min in a water bath, followed by centrifugation at 1160 × g for 15 min in a laboratory centrifuge. The supernatant containing the proteins was stored at 10C until used.

Spray Drying

The protein dispersion was heated to 70C and then passed through cheesecloth to remove traces of sediments. It was then subjected to spray drying

in a B-190 mini spray dryer (Büchi Laboratoriums-Technik, Flawil-Schweiz, Switzerland). The feed rate was 0.5 L/h with inlet and outlet temperatures of 200 and 90C, respectively.

Proximate Analysis of the Protein Powder

Spray dried powder prepared from two separate batches was used for analysis. Replicate samples of the powder were analyzed for nitrogen content, fat, moisture and ash contents using standard methods (AOAC 1980). Crude protein was expressed as % N × 6.25.

Functional Properties

For the determination of functional properties, the method of Lowry *et al.* (1951) was employed to determine protein and tyrosine, using bovine albumin and 1-tyrosine, respectively.

The determination of protein solubility was based on the method of Messinger *et al.* (1987). The protein powder, at concentrations ranging from 1 to 5% (w/v), was dispersed in distilled water and shaken for 30 s using a Vortex-Genie. Aliquots of the dispersions were centrifuged in an Eppendorf (5415 C) centrifuge for 5 min at 1000 rpm. Solubility was expressed as the percent of total protein remaining in the supernatant.

Emulsification capacity was measured according to the procedure of Rasekh and Metz (1973). A mixture of 25 ml of peanut oil and 20 ml of water or 3% NaCl in water, containing 0.5–2.5 mg protein powder per ml, was homogenized using a Janke and Kunkel (IKA-labortechnik, Germany) homogenizer at a speed of 9,500 rpm for 1 min. The homogenate was centrifuged for 30 min at 1160 × g and the volume of oil separated was measured. In order to determine the emulsion stability, the emulsion was heated in a water bath at 80C for 30 min. It was cooled to room temperature and centrifuged at 1160 × g for 15 min, and the volume of oil separated was measured. In the unheated emulsions, the percent of unseparated oil gave the index of emulsifying capacity, while in the heated emulsions it gave the index of emulsion stability.

The emulsifying activity index was determined using the method of Huang and Kinsella (1987). A mixture consisting of 100 mg of the powder in 20 ml of 0.1M phosphate buffer (pH ranging from 6.7 to 8.5) and 20 ml of soybean oil was homogenized for 30 s in a Janke and Kunkel (IKA-labortechnik, Germany) homogenizer at a speed of 9,500 rpm. The homogenate was diluted 100-fold in a 0.1% aqueous solution of sodium dodecyl sulfate, and the turbidity was measured at 550 nm.

The trypsin digestibility of the powder was determined by measuring the extent of tyrosine release when the powder was digested with trypsin. The ratio of powder to trypsin was 50:1 (w/w). For this, 25 mg of the powder in 25 ml of 0.1 M sodium phosphate buffer (pH 8.0) were incubated with trypsin (Sigma, 10100 units/mg activity) at 50C. At intervals, aliquots were pipetted into 15% (w/v) aqueous trichloroacetic acid, centrifuged at 5000 rpm for 10 min in an Eppendorf centrifuge, and the tyrosine contents of the supernatants were determined as indicated above.

The apparent viscosity of washed mince homogenate in water was measured with a Brookfield synchro-lectric viscometer using spindle #2 or #3 at a speed of 60 rpm, while that of dispersions of the powder in water at a concentration of 1% was determined by a Brookfield digital viscometer, model RV, using spindle CP-40 at varying shear rates.

Wettability was determined by noting the time required for 1 g of the powder to become completely wet when suspended in tap water. Hygroscopicity was determined by noting the increase in weight when the powder (1 g) was kept open to air at 62% relative humidity and 24C for four days.

RESULTS AND DISCUSSION

The mechanically deboned mince had a moisture content of 86% and was dark in color. The washing treatment resulted in the removal of significant amounts of soluble compounds as well as odor-bearing compounds and lipids. It yielded a light brown-colored mince having a moisture content of 88–90%. About 30% of the total nitrogenous compounds were lost during the washing process (Venugopal et al. 1994). For washing, NaCl and NaHCO$_3$ were employed to facilitate the removal of lipids and to enhance the hydrophillic nature of the washed protein (Suzuki 1981). It was found that bicarbonate washing gave dispersions having higher apparent viscosity, suggesting enhanced affinity of the protein for water. When the washed mince was dispersed in an equal amount of cold water by the procedure described, the dispersion had high apparent viscosity. This was reduced almost completely after heat treatment. The loss of viscosity, which could be due to conformational changes of the protein, was comparable with that of other proteins (Rao 1977). It was observed that homogenization of the washed mince in quantities of water less than the amount of the mince gave thick dispersions that retained appreciable viscosity even after heating, and hence were not suitable for spray drying. For example, the homogenate at 30% mince concentration had an apparent viscosity of 3300 cps, which was reduced to 40 cps after heating while protein solubility was not affected. The extractability of the washed mince in water was as high as 92%,

and the extract contained about 5% solids. The low viscosity of the dispersion (about 40 cps), its ability to hold protein in solution and its thermostability (Venugopal *et al.* 1994) made spray drying feasible. The thermostable nature of the dispersion was made use of by inactivating the residual protease in it and by pasteurizing it, giving the dispersion a refrigerated shelf-life of up to 10 days, thereby facilitating convenient spray drying.

TABLE 1.
PHYSICAL PROPERTIES OF WASHED CAPELIN MINCE DISPERSION AND
SPRAY DRIED PROTEIN CONCENTRATE

Dispersion	Protein Concentrate	
Dark color, if not bleached	Off-white color	
Off-white color after bleaching with H_2O_2	Insignificant fishy odor	
Solid content, 5 %	Protein:	84.61 ± 0.66 %
Apparent Viscosity, 40 cps	Lipid:	4.00 ± 0.05 %
Stable to heat (80 C)	Ash:	3.43 ± 0.09 %
	pH:	7.10 ± 0.05 (1 % suspension)
	Wettability:	good
	Hygroscopicity:	nil

Table 1 lists the physical properties of the dispersion and of the spray dried powder. Grading the wettability of the powder as "good" means that the powder became completely wet within 2 min when it was suspended in tap water. The color of the spray dried powder can be improved by the addition of 2% (v/v) of 30% H_2O_2 to the dispersion and heating it to 70C before spray drying. The powder was not hygroscopic, since no increase in weight was noticed when it was kept open to the air for four days at 62% relative humidity and 24C.

The powder was significantly soluble in water as well as in 3% NaCl (Fig. 1). It did not have significant apparent viscosity, as shown in Fig. 2. The apparent viscosity decreased with an increase in shear rate. It was of interest to examine some functional properties of the powder, since these properties are
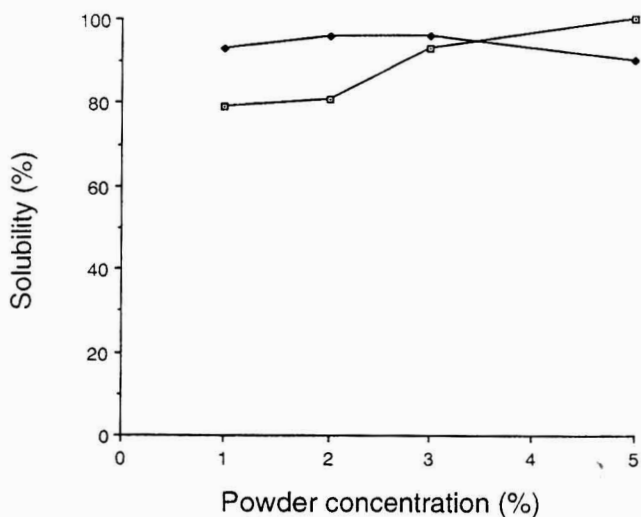
FIG. 1. SOLUBILITY OF CAPELIN PROTEIN POWDER
IN WATER AS A FUNCTION OF CONCENTRATION
♦, Batch 1; □, Batch 2.
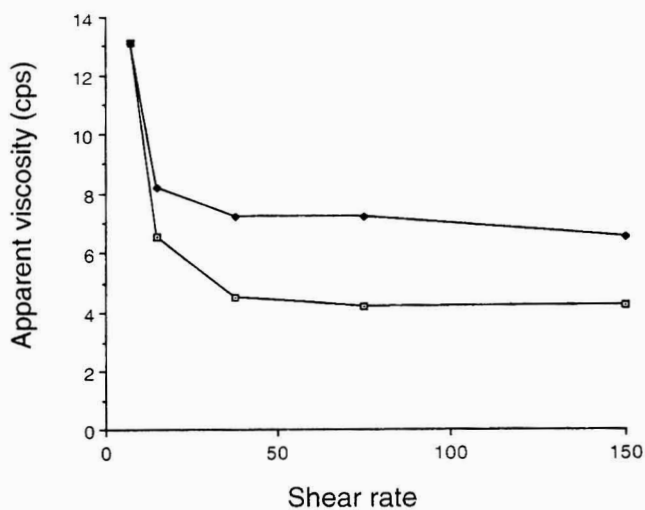
FIG. 2. APPARENT VISCOSITY OF 1% (W/V) CAPELIN PROTEIN
CONCENTRATE IN WATER AS A FUNCTION OF SHEAR RATE
♦, Batch 1; □, Batch 2.

TABLE 2.
OIL EMULSIFYING CAPACITY OF CAPELIN PROTEIN CONCENTRATE

Protein, mg / ml	Percent oil emulsified			
	In water		In 3 % NaCl	
	Batch 1	Batch 2	Batch 1	Batch 2
0.5	28	28	28	28
1.0	40	60	80	60
1.5	66	92	88	92
2.5	88	96	92	96

TABLE 3.
EMULSION STABILITY OF CAPELIN PROTEIN CONCENTRATE

Protein, mg / ml	Percent oil emulsified			
	In water		In 3 % NaCl	
	Batch 1	Batch 2	Batch 1	Batch 2
1.5	36	40	36	40
2.5	60	64	72	74

interrelated in the production of fabricated foods (Kinsella 1982). These properties include oil emulsification, whippability, texturization and water and oil absorptivity. The oil emulsification capacity of the powder is presented in Table 2. At and above a concentration of 1 mg/ml, more than 80% of the oil was emulsified, suggesting appreciable oil emulsification capacity. The prepared emulsions retained 36–40% of the oil after heat treatment at 80C for 30 min (Table 3).

The emulsion activity index (EAI) of the powder at varying pH values is presented in Fig. 3. The powder showed appreciable EAI at pH values above neutral. However, at pH 6.7 the value was lower, possibly due to low solubility of the protein at lower pH values (Venugopal et al. 1994).

Trypsin digestibility of the capelin powder is depicted in Fig. 4. It can be seen that the protein was easily digestible by trypsin as indicated by the appreciable liberation of tyrosine over a period of 15 min.
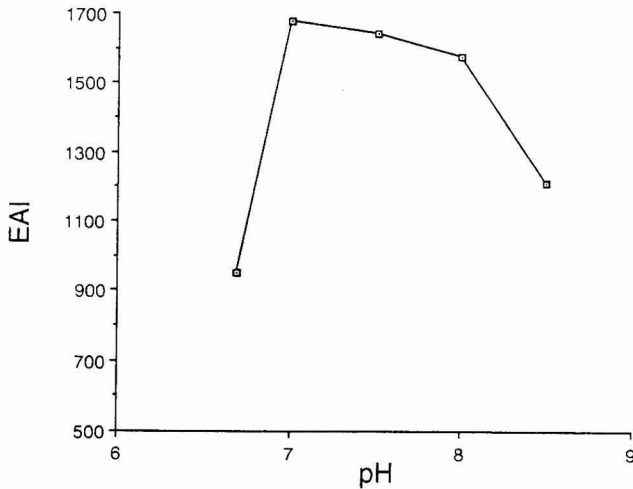
FIG. 3. EMULSION ACTIVITY INDEX (EAI) OF CAPELIN
PROTEIN CONCENTRATE AT VARYING pH VALUES
Sample from Batch 2 was used.
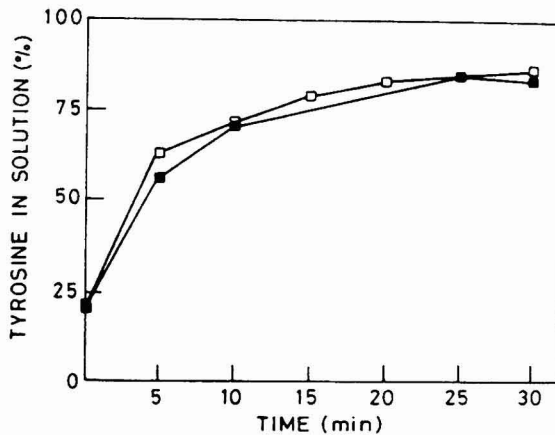
FIG. 4. TRYPSIN DIGESTIBILITY OF CAPELIN PROTEIN
CONCENTRATE AS A FUNCTION OF TIME
■, Batch 1; □, Batch 2.

These results suggest the feasibility of converting capelin into a protein powder possessing good functional properties by the spray drying process. In comparison to its use with such food items as dairy products and fruit juices, spray drying has so far found limited scope in seafood processing, essentially due to an inability to prepare fish proteins in a soluble, low viscosity,

ready-flowing state required for spray drying. Applications in which fish proteins could be modified to enhance their solubility and hence their amenability for spray drying include concentrating protein hydrolysates from fish and krill, and dehydrating stick water, a by-product of the fishmeal industry (Masters 1972; Kubota *et al.* 1985; Yu and Tan 1992). In the present work, it could be expected that the dissolution of the washed myofibrillar protein in water had been achieved by making use of the gel-forming ability of washed fish muscle (Suzuki 1981). The solubilized proteins formed a dispersion with remarkable thermostability (Venugopal *et al.* 1994), facilitating its dehydration. Apparently, spray drying of whole fish protein has been attempted by only one group (Niki *et al.* 1982a,b), who prepared functionally active fish protein powder from Alaska pollock. The dressed fish was minced and milled in a colloidal mill along with saccharides, which were added to prevent protein denaturation. The slurry was spray dried to obtain a product containing 65% protein, 4% fat and 24% saccharides. The authors overcame the problem of high feed viscosity by adding carbonic acid. In contrast, the present process resulted in the conversion of washed capelin muscle into a low-viscosity water dispersion. This dispersion was amenable to spray drying, producing a concentrate of up to 85% protein without requiring any additive.

Fish proteins are known to be very unstable, undergoing rapid denaturation associated with loss of solubility and functional properties, depending upon the processing conditions. Thus, fish protein concentrate (FPC) prepared by hot solvent extraction of fish meat is sparingly soluble in water and has poor functional properties (Sikorski and Naczk 1981). Solubility of proteins is correlated with such functional properties as oil emulsification, foaming capacity and gelation (Kinsella 1976, 1982). In contrast to the conventional FPC prepared by solvent extraction, the spray dried capelin powder was highly soluble in water and had appreciable functionality. The oil emulsification capacity of the capelin powder was higher than those reported not only for wheat and soy flours and sunflower proteins but also for squid muscle proteins, which have an absorption value of 30 ml of oil per 100 g (Kinsella 1976). The capelin powder emulsion was also stable to heating. These properties provide the preparation with the potential for use as a protein supplement and as an extender in cereal-based products. These possibilities have been discussed recently (Venugopal and Shahidi 1994).

ACKNOWLEDGMENTS

REFERENCES

ANDREWS, R. 1988. The capelin fishery stability in the future. An assessment of the industry and a plan for future development and management. Department of Fisheries, Government of Newfoundland and Labrador, Canada.

AOAC. 1980. *Official Methods of Analysis,* 13th Ed. (W. Horwitz, ed.), Assoc. of Official Analytical Chemists, Washington, DC.

EIDE, O., BORRENSEN, T. and STRÖM, T. 1982. Minced fish production from capelin *(Mallotus villosus).* A new method for gutting, skinning and removal of fat from small fatty species. J. Food Sci. *47,* 347–349.

FINCH, R. 1977. Whatever happened to fish protein concentrate? Food Technol. *31*(5), 44–53.

HUANG, V.T. and KINSELLA, J.E. 1987. Effect of phosphorylation on emulsifying and foaming properties and digestibility of yeast protein. J. Food Sci. *52,* 1684–1688.

JAMES, D. 1992. Seafood technology in the 90's: The needs of developing countries. In *Seafood Science and Technology*, (E.G. Bligh, ed.) pp. 12–23, Fishing News Books, London.

KINSELLA, J.E. 1976. Functional properties of food proteins. A survey. CRC Crit. Rev. Food Sci. Nutr. *9,* 219–338.

KINSELLA, J.E. 1982. Relationships between structure and functional properties of food proteins. In *Food Proteins*, (P.F. Fox and J.J. Condon, eds.) p. 51, Applied Science Publishers, New York.

KUBOTA, K., TAKASAKI, S., KOBAYASHI, A. and AKATSUKA, S. 1985. Aroma of new seasoning. 1. Changes of aroma constituents of krill hydrolysate during spray drying. J. Jap. Soc. Food Sci. Technol. *32,* 765–768.

LOWRY, O.H., ROSEBROUGH, N.J., FARR, A.L. and RANDALL, R.J. 1951. Protein measurement by Folin phenol reagent. J. Biol. Chem. *193,* 265–275.

MASTERS, K. 1972. *Spray Drying. An Introduction to Principles, Operational Practices and Applications*, pp. 606–613, Leonard Hill Books, London.

MESSINGER, J.K., RPONOW, J.H., ZEECE, M.G. and ANDERSON, R.L. 1987. Effect of partial proteolysis and succinylation on functionality of corn germ protein isolate. J. Food Sci. *52,* 1620–1624.

NIKI, H., DEYA, L., KATO, T. and IGARASHI, S. 1982a. Studies related to development of a spray drying method for making active fish protein powder. I. The process of producing active fish protein powder. Bull. Jap. Soc. Sci. Fish. *48*, 999–1004.

NIKI, H., DEYA, L., KATO, T. and IGARASHI, S. 1982b. Studies related to development of a spray drying method for making active fish protein powder. II. Some factors in the production of active fish protein powder. Bull. Jap. Soc. Sci. Fish. *48*, 1133–1137.

RAO, M.A. 1977. Rheology of liquid foods. J. Texture Studies *8*, 135–168.

RASEKH, J. and METZ, A. 1973. Acid precipitated fish protein isolate exhibits good functional properties. Food Prod. Dev. *7*, 18–24.

SIKORSKI, Z.E. and NACZK, M. 1981. Modifications of technological properties of fish protein concentrate. CRC Crit. Rev. Food Sci. Nutr. *14*(3), 201–230.

SUZUKI, T. 1981. *Fish and Krill Protein: Processing Technology*, Elsevier Applied Science, London.

VENUGOPAL, V. 1992. Mince from low cost fish species. Trends Food Sci. Technol. *3*, 2–5.

VENUGOPAL, V., MARTIN, A.M. and PATEL, T.R. 1994. Extractability and stability of washed capelin *(Mallotus villosus)* muscle in water. Food Hydrocolloids (In press).

VENUGOPAL, V. and SHAHIDI, F. 1994. Value added products from underutilized fish species. CRC Crit. Rev. Food Sci. Nutr. (In press).

YU, S.Y. and TAN, L.K. 1990. Acceptability of crackers ("keropok") with fish protein hydrolysate. Int. J. Food Sci. Technol. *25*, 204–208.

WHITTLE, K.J. and HARDY, R. 1992. Under-used resources. Recent process innovations. In *Seafood Science and Technology*, (E.G. Bligh, ed.) pp. 101–115, Fishing News Books, London.

AUTHOR INDEX

SUBJECT INDEX

UNITED STATES POSTAL SERVICE™

Statement of Ownership, Management, and Circulation
(Required by 39 U.S.C. 3685)

1. Publication Title	2. Publication No.	3. Filing Date
Journal of Food Processing and Preservation	0 - 5 6 - 4 7 0	October 1, 1994

4. Issue Frequency	5. No. of Issues Published Annually	6. Annual Subscription Price
Bimonthly	6	$143.00

7. Complete Mailing Address of Known Office of Publication (Street, City, County, State, and ZIP+4) (Not Printer)
2 Corporate Drive, POB 374
Trumbull, Fairfield, Connecticut 06611-0374

8. Complete Mailing Address of Headquarters or General Business Office of Publisher (Not Printer)
2 Corporate Drive, POB 374
Trumbull, Connecticut 06611-0347

9. Full Names and Complete Mailing Addresses of Publisher, Editor, and Managing Editor (Do Not Leave Blank)
Publisher (Name and Complete Mailing Address)
John J. O'Neil
2 Corporate Drive, POB 374
Trumbull, CT 06611

Editor (Name and Complete Mailing Address)
Dr. Daryl B. Lund
Rutgers-The State University
104 Martin Hall, POB 231, New Brunswick, NJ 08903

Managing Editor (Name and Complete Mailing Address)
None

10. Owner (If owned by a corporation, its name and address must be stated and also immediately thereafter the names and addresses of stockholders owning or holding 1 percent or more of the total amount of stock. If not owned by a corporation, the names and addresses of the individual owners must be given. If owned by a partnership or other unincorporated firm, its name and address as well as that of each individual must be given. If the publication is published by a nonprofit organization, its name and address must be stated.) (Do Not Leave Blank.)
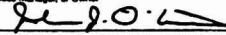
Full Name	Complete Mailing Address
Food & Nutrition Press, Inc.	2 Corporate Drive, POB 374, Trumbull, CT 06611
John J. O'Neil	53 Stonehouse Road, Trumbull, CT 06611
Michael J. Tully	3 N. Slope, Union Gap, Clinton, NJ 08809
Kathryn B. Christopher Ziko	8 Maria Alicia Dr., Huntington, CT 06484
John J. O'Neil, Jr.	115 Maureen St., Stratford, CT 06497

11. Known Bondholders, Mortgagees, and Other Security Holders Owning or Holding 1 Percent or More of Total Amount of Bonds, Mortgages, or Other Securities. If none, check here. ☐ None

Full Name	Complete Mailing Address
None	

13. Publication Name	14. Issue Date for Circulation Data Below
Journal of Food Processing & Preservation	10-13-93,11-24-93,1-10-94,4-20-94,6-29-94,8-17-9

15. Extent and Nature of Circulation	Average No. Copies Each Issue During Preceding 12 Months	Actual No. Copies of Single Issue Published Nearest to Filing Date
a. Total No. Copies (Net Press Run)	500	500
b. Paid and/or Requested Circulation (1) Sales Through Dealers and Carriers, Street Vendors, and Counter Sales (Not Mailed)	0	0
(2) Paid or Requested Mail Subscriptions (Include Advertisers' Proof Copies/Exchange Copies)	314	320
c. Total Paid and/or Requested Circulation (Sum of 15b(1) and 15b(2))	314	320
d. Free Distribution by Mail (Samples, Complimentary, and Other Free)	43	43
e. Free Distribution Outside the Mail (Carriers or Other Means)	0	0
f. Total Free Distribution (Sum of 15d and 15e)	43	43
g. Total Distribution (Sum of 15c and 15f)	357	363
h. Copies Not Distributed (1) Office Use, Leftovers, Spoiled	143	137
(2) Return from News Agents	0	0
i. Total (Sum of 15g, 15h(1), and 15h(2))	500	500
Percent Paid and/or Requested Circulation (15c / 15g x 100)	88%	88%

16. This Statement of Ownership will be printed in the ___Vol. 18 No. 6___ issue of this publication. ☐ Check box if not required to publish.

17. Signature and Title of Editor, Publisher, Business Manager, or Owner
John J. O'Neil, Publisher   Date Oct. 1, 1994

I certify that all information furnished on this form is true and complete. I understand that anyone who furnishes false or misleading information on this form or who omits material or information requested on the form may be subject to criminal sanctions (including fines and imprisonment) and/or civil sanctions (including multiple damages and civil penalties).

Instructions to Publishers

1. Complete and file one copy of this form with your postmaster on or before October 1, annually. Keep a copy of the completed form for your records.

2. Include in items 10 and 11, in cases where the stockholder or security holder is a trustee, the name of the person or corporation for whom the trustee is acting. Also include the names and addresses of individuals who are stockholders who own or hold 1 percent or more of the total amount of bonds, mortgages, or other securities of the publishing corporation. In item 11, if none, check box. Use blank sheets if more space is required.

3. Be sure to furnish all information called for in item 15, regarding circulation. Free circulation must be shown in items 15d, e, and f.

4. If the publication had second-class authorization as a general or requester publication, this Statement of Ownership, Management, and Circulation must be published; it must be printed in any issue in October or the first printed issue after October, if the publication is not published during October.

5. In item 16, indicate date of the issue in which this Statement of Ownership will be printed.

6. Item 17 must be signed.

Failure to file or publish a statement of ownership may lead to suspension of second-class authorization.

PS Form 3526, October 1994 (Reverse)

GUIDE FOR AUTHORS

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

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

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

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

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

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

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

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

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

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

RIZVI, S.S.H. 1986. Thermodynamic properties of foods in dehydration. In *Engineering Properties of Foods*, (M.A. Rao and S.S.H. Rizvi, eds.) pp. 133–214, Marcel Dekker, New York.

MICHAELS, S.L. 1989. Crossflow microfilters ins and outs. Chem. Eng. *96*, 84–91.

LABUZA, T.P. 1982. *Shelf-Life Dating of Foods,* pp. 66–120, Food & Nutrition Press, Trumbull, CT.

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

Tables should be numbered consecutively with Arabic numerals. Type tables neatly and correctly as they are considered art and are not typeset. The title of the table should appear as below:

TABLE 1.

ACTIVITY OF POTATO ACYL-HYDROLASES ON NEUTRAL LIPIDS, GALACTOLIPIDS AND PHOSPHOLIPIDS

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

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

Acknowledgments: Acknowledgments should be listed on a separate page.

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

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

EDITORIAL OFFICE: DR. D.B. Lund, *Journal of Food Processing and Preservation*, Rutgers, The State University, 104 Martin Hall, P.O. Box 231, New Brunswick, New Jersey 08903 USA.

CONTENTS